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X-RAY CRYSTALLOGRAPHY

X-RAY CRYSTALLOGRAPHY

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WITH 29 DIAGRAMS

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GENERAL PREFACE

THIS series of small monographs is one which should commend itself to a wide field of readers.

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O. W. RICHARDSON

KING'S COLLEGE
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PREFACE

IN this book I have tried to give an outline of the main principles underlying the methods of analysing crystals by means of X rays, which may be of interest, as a general account, to students of other branches of physics, and at the same time serve as an introduction to the subject for those about to take up its study seriously. Detailed examples of the analysis of simple crystals are now to be found in a number of text-books, and an adequate treatment of more complicated cases would have been impossible in the somewhat limited space at my disposal. I have thought it better, therefore, to deal on the whole with general methods rather than with their application to particular cases, hoping that the account given may stimulate the reader to consult the original sources.

My indebtedness to many other works will be plain, and reference is made to some of them in the Bibliography. All writers on this subject must in particular owe much to *X-Rays and Crystal Structure*, by W. H. and W. L. Bragg, to Ewald's admirable book *Kristalle und Röntgenstrahlen*, and to Niggli's *Geometrische Kristallographie des Diskontinuums*. My thanks are due to Professor W. L. Bragg, F.R.S., who kindly read the manuscript and made a number of valuable suggestions; to Mr. Herbert Bell, M.A., through whose criticisms certain obscurities have been, I hope, removed; and to the Royal Society for permission to reproduce Fig. 28, which was first published in their Proceedings.

R. W. J.

PHYSICAL LABORATORIES

THE UNIVERSITY OF MANCHESTER

March, 1930

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X-RAY CRYSTALLOGRAPHY

CHAPTER I

CRYSTAL FORM AND THE SPACE-LATTICE

INTRODUCTION

THE regular geometrical form of a crystal is a consequence of the regular arrangement of the molecules of which it is built up. The regularity is that of a 3-dimensional pattern, in which a certain unit of structure is repeated over and over again in space, just as the regularity of a wall-paper is due to the repetition of a certain design in two dimensions. It had long been recognized that a theory of this type would account for the observed facts of crystalline form and symmetry, and the geometry of such space-patterns had been fully worked out, but it was not until the development of X-ray crystallography that it became possible to determine the actual nature of the unit, and of the pattern in any crystal. In the sixteen years which have passed since the discovery of the method by v. Laue, and the publication of the first analyses of crystal structures by W. L. Bragg, much progress has been made, and it is now clear that the type of regular arrangement formerly associated only with definite crystals is characteristic of all true solids, and that the study of crystal structure is really the study

of the architecture of matter in the solid state. X-ray crystallography is descended from, and constantly uses, the results of the older crystallography, and it will therefore be necessary at the outset to deal briefly with a few of the more important principles of the parent science.

GENERAL PROPERTIES OF CRYSTALS

A single crystal is homogeneous, in the sense that it has identical properties at all points within it ; it is not in general, however, isotropic ; that is to say, that directed properties, such as thermal or electrical conductivity, or the coefficient of thermal expansion, or the velocity of propagation of light within the crystal, depend upon the direction in the crystal which is being considered. Parallel to any given direction, the properties at all points in the crystal are the same, but, at any one point, the same property differs in different directions. This suggests at once a regularity in the internal structure of the crystal, for, if the arrangement of its constituent molecules were entirely at random, it is clear that we could not have such a dependence of properties on direction. It is this internal regularity of structure which is the essential characteristic of the crystalline state, and not the external regularity of form : the latter, however, is a direct consequence of the former, and from it we may get the first hint as to the nature of the internal structure.

CRYSTAL FORM AND THE LAW OF RATIONAL INDICES

Before proceeding further, it is desirable to give greater precision to the idea of crystal form. Let us consider, for example, what is meant by the statement that potash alum crystallizes in regular octahedra. It is true that a crystal of alum may grow in such a way that its bounding faces do form a regular octahedron, but, unless special precautions are taken, the crystal will probably have eight faces of different sizes, and may not at first sight bear any resemblance to a regular

octahedron. The essential point is that whatever the relative sizes of the faces, and whatever the actual shape of the crystal, the angles between the faces are always those between the faces of a regular octahedron. Or, to put it in another way, the crystal may always be set so that its eight faces are parallel to those of a regular octahedron.

It is thus the directions of the faces and not the shape of the crystal which is the essential matter. From any point within a crystal let perpendiculars be drawn to the faces, supposed produced if necessary. The radiating bundle of normals so obtained is independent of the size and shape of the faces, and depends only on their directions; it is thus characteristic of the form of a crystal on which a certain set of faces is developed, and is a much better description of it than its actual shape would be, since this depends so greatly on the accidents of growth. We may if we like suppose a sphere described about the origin of the normals, and intersecting them in a set of points which will again be independent of all but the directions of the faces. When a crystallographer speaks of the geometrical form of a crystal, it is really this radiating set of normals, or the corresponding array of points on the sphere, which he has in mind.

The eight faces corresponding to the octahedron are said to constitute a **form**. A crystal may have more than one form developed at the same time: an alum crystal might, for example, have six faces corresponding to those of a cube, as well as the octahedral faces: but, for the same crystal, the relative directions of the faces of the different forms are fixed, and very definite rules, which we must now consider, govern the directions which are possible.

It is first of all necessary to choose a set of axes, fixed in the crystal, to which the directions of the faces can be referred, and, for this purpose, three lines parallel to the lines of intersection of three faces which do not lie in the same plane are used. In theory, any three

such faces will serve, but in practice there is usually some set of axes which suggests itself as the most convenient. In a cubic crystal, for example, three edges of the cube, giving a set of rectangular axes, would always be chosen.

Three faces thus define the axes ; we must now take a fourth face, which must cut all three axes, as a standard plane. Let ABC (Fig. 1) be such a plane, and

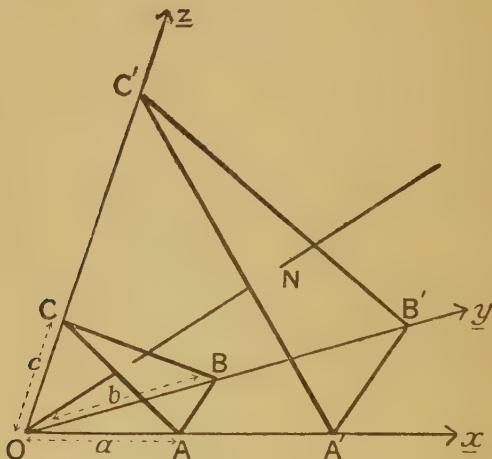


FIG. 1

let it make intercepts $OA (= a)$, $OB (= b)$, $OC (= c)$, on the axes Ox , Oy , Oz , respectively. The experimental law which is found to govern the directions of the other faces of the crystal can now be stated as follows :

A face which is parallel to a plane whose intercepts on the three axes are Ha , Kb , Lc , where H , K , and L are whole numbers, is a possible face of the crystal, and for the planes which commonly occur, H , K , and L are small whole numbers.

For all planes parallel to a given direction, the ratio

of the intercepts on the axes is the same, so that if $A'B'C'$ be a possible crystal face, we have, from the rule given above,

$$OA' : OB' : OC' = Ha : Kb : Lc = a/KL : b/LH : c/HK \\ = a/h : b/k : c/l \quad (1)$$

where h, k, l , are again small whole numbers. The numbers h, k, l , define the plane, to which a symbol (hkl) may be given, and are called its Miller indices, after Miller who introduced them. The Miller indices are always whole numbers, and for the commonly occurring faces of a crystal, small whole numbers, and the law which we have just considered is known as the **Law of Rational Indices**.

For a given value of the ratio $a : b : c$, the Miller indices of a plane are inversely proportional to its intercepts on the axes. The geometrical reason for using them rather than the numbers H, K, L , which are directly proportional to the intercepts, is that $h/a, k/b, l/c$, are proportional to the direction cosines of the normal to the plane (hkl), and, as we have seen, it is the normal to the plane which is used to define it crystallographically. The proportionality follows at once from equation (1), for if λ, μ, ν are the direction cosines of the normals to the plane $A'B'C'$ (Fig. 1), that is to say the cosines of the angles which the normal makes with the axes of x, y , and z respectively, and p is the length of the perpendicular, ON , from the origin to the plane, we have $p = \lambda \cdot OA' = \mu \cdot OB' = \nu \cdot OC'$, and hence, from equation (1), $\lambda : \mu : \nu = h/a : k/b : l/c$.

There is the further advantage that when a plane is parallel to one of the axes, and the corresponding intercept becomes infinite, the Miller index becomes zero. The ratio $a : b : c$ is known as the axial ratio of the crystal. In purely crystallographic work, b is usually made equal to unity, a and c being then in general not integers. The value of the axial ratio depends upon the choice of the standard plane, and is thus to some extent arbitrary. We shall find later, however, that a physical

interpretation can be given to the numbers a , b , c , and that this arbitrariness will in some degree disappear.

The indices of the standard plane are always (111): in giving those of the other planes it is customary to express them so that they contain no common factor. In the case of the alum crystal considered above we shall take the axes parallel to the intersections of the cube faces. One of the octahedral faces will then be taken as the standard plane; its indices will be (111), and, since it makes equal intercepts on the three axes, we have $a = b = c$. The face of the octahedron opposite to that chosen as standard will, if the origin is chosen within the crystal, make negative intercepts on all three axes, or, more generally, the direction cosines of its normals will all be negative. The indices are therefore negative, and the symbol of the face is written ($\bar{1} \bar{1} \bar{1}$), the negative sign, for the sake of compactness, being put above the corresponding figure. The symbols of the eight faces of the octahedron are (111), (1 $\bar{1}$ 1), ($\bar{1}$ 11), ($\bar{1} \bar{1}$ 1), (1 $\bar{1} \bar{1}$), (11 $\bar{1}$), ($\bar{1}$ 1 $\bar{1}$), ($\bar{1} \bar{1} \bar{1}$), and the symbol for the whole set of faces, or the *form*, is {111}. In a similar way, the symbol for the cube form is {100} and that for the set of twelve planes containing an axis and a cube diagonal, the dodecahedral form, is {110}. One zero always occurs in the symbol for a face which is parallel to an axis, and two in that of one which is parallel to one of the axial planes.

THE LAW OF RATIONAL INDICES AND THE SPACE-LATTICE

The law of rational indices follows very simply if we assume the crystal to be built up by stacking identical units in a 3-dimensional pattern. Such a pattern will possess the homogeneity which we have seen to be one of the principal characteristics of a crystal, for each unit is similar and similarly situated, and, if we suppose the extension of the pattern to be infinite, no unit is in any way to be distinguished from any other.

It will be easiest first of all to consider a pattern in

two dimensions, such as a wall-paper pattern. Its essential characteristic is that it is produced by continued repetition of a single 'unit', and that, in the completed pattern, such units must lie in rows, equally spaced, so that corresponding points of the units lie at the points of intersection of two sets of equally spaced parallel lines. For, since all the units are to be identical and identically placed, if a point in one unit, A_{10} in Fig. 2, lies in a certain direction, and at a certain distance a , from a corresponding point A_{00} in another unit, there

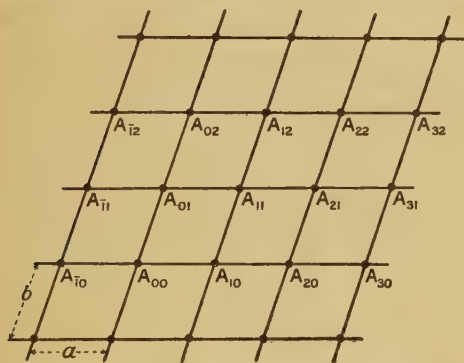


FIG. 2

Two-dimensional lattice.

must be a corresponding point A_{20} in the same direction and at the same distance from A_{10} , and so on indefinitely in both directions. Thus $A_{00}A_{10}A_{20} \dots$ lie in the same straight line, and $A_{00}A_{10} = A_{10}A_{20} = A_{20}A_{30} \dots = a$. Similarly, if in any other direction from A_{00} there is a point A_{01} at a distance b , there must be other points, $A_{02}, A_{03} \dots$ collinear with A_{00} and A_{01} and equally spaced. Moreover, there must be rows of points along lines passing through $A_{10}, A_{20}, A_{30} \dots$ parallel to the row $A_{00}A_{01}A_{02} \dots$ and with exactly the same spacing. Thus the collection of points taken altogether forms a regular mesh, or net-plane.

If we extend this idea to three dimensions, we shall have a row of points through A_{00} all equally spaced in some third direction, not in the same plane as A_{10} and A_{01} , and similar, parallel, rows of points through every one of the points in the original net-plane, the whole collection of points being formed by the intersections of three sets of parallel and equally spaced planes. Such a collection of points is called a **space-lattice**.

Fig. 3 represents a small part of such a space-lattice. We may take any point O as origin of co-ordinates, and

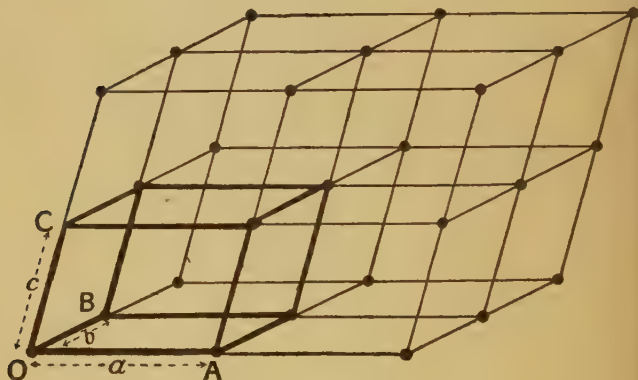


FIG. 3
Space-lattice.

take as axes three directions OA , OB , OC , which are the directions of three rows of points not lying in the same plane. Let A , B , C be the positions of three points adjacent to O , and such that no other points lie inside the parallelepiped of which OA ($= a$), OB ($= b$), and OC ($= c$) are three edges. Such a parallelepiped is said to be a **unit cell** of the lattice, and the distances a , b , and c its **primitive translations**. The co-ordinates of any point of the lattice, referred to the origin and axes considered, are (ma, nb, pc) where m ,

l, p are any whole numbers positive or negative. The primitive translations of the lattice may be chosen in an indefinite number of ways. The corresponding unit cell will always have the same volume, although its shape will vary. The whole lattice may be built up by tacking together such unit cells, the lattice points lying at the common corners. There is **one** lattice point per unit cell, for, although the cell has eight corners, eight cells meet at each corner, and only an eighth of a point belongs to each cell.

THE LATTICE PLANES

In a space-lattice, all the points may be included in a set of parallel and equally spaced **planes**, each of which is a net-plane. Such a set of planes may be chosen in an indefinite number of ways; if each plane of the set is densely occupied by points, the planes will be widely spaced; if they are sparsely occupied, they will be close together. If we consider a crystal as formed of similar units arranged in a space-lattice, it will be seen that planes can be chosen in the crystal which contain a large number of units closely packed, and that these planes are comparatively widely separated. Such planes might well form the natural boundaries to the collection of units, in other words, the faces of the crystal. The more sparsely occupied planes have much less physical reality; they exist mathematically, but there is no reason to suppose that they will form crystal faces. We shall see that this idea leads at once to the law of rational indices.

For simplicity, we return to two dimensions. The analogues of the planes in the space-lattice are now rows of points. Let any two important directions, OA, OB, in Fig. 4, be chosen as axes, and let the primitive translations be a and b . Rows of points may be chosen in directions other than those of the axes, and we notice that their intercepts on the axes are always integral multiples of a and b , say ma and nb , and further, that the densely occupied rows are always those for which

the ratio $m : n$ is a ratio of small whole numbers. Thus, if we assign indices to the rows analogous to the Miller indices for planes, which are proportional to the reciprocals of the intercepts of the rows on the axes, these

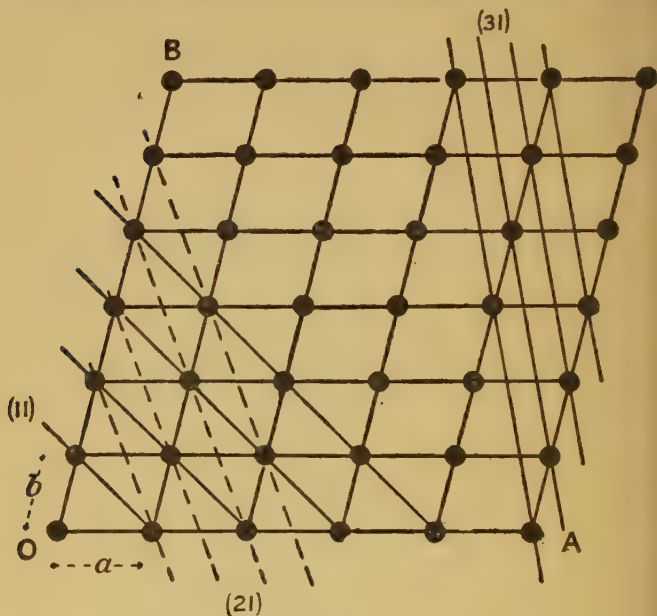


FIG. 4

Rows of points in a 2-dimensional lattice.

indices will be small whole numbers for the principal rows.

Extending this once more to three dimensions, we see that the planes which contain a large number of lattice points per unit area are those whose intercepts on the axes are ma , nb , pc , where $m : n : p$ is the ratio of three small whole numbers. That is to say, they are planes for which the law of rational indices holds.

The idea of the space-lattice as underlying the structure of crystals was first worked out in detail by Bravais many years ago. The unit of crystal structure, molecule or atom, or group of molecules or atoms, was supposed to lie at the point of a space-lattice, and the complete structure to be built up from the unit simply by applying to it over and over again the lattice translations. We must now see how the application of X rays to the problem enables us to demonstrate the actual existence of these space patterns and to determine their arrangement.

CHAPTER II

THE CRYSTAL LATTICE AS A DIFFRACTION GRATING

INTRODUCTION

THE important discovery of von Laue which made it possible to investigate crystal structure by means of X rays was based directly on the idea of the crystal as a repeating pattern in space. It is well known that if a beam of light falls on a screen perforated with holes arranged in a regular pattern whose spacings are comparable with the wave-length of the light, diffraction occurs; the light, after passing through the screen, consists not only of a somewhat weakened beam in the direction of the incident light, but also of other, regularly arranged, separate beams, deviated from the original direction through angles depending on the ratio of the wave-length of the light to the spacings of the pattern. If both the wave-length and the scale of the pattern are diminished, so as to keep this ratio the same, the diffraction pattern, apart from changes in intensity, remains unaltered. The diffraction is due to the interaction of the regularly periodic pattern with the regularly periodic light waves.

If a crystal consists of the repetition of similar units in a regular pattern, we might perhaps expect to get diffraction when a beam of light is passed through it. The crystal pattern, however, repeats itself several thousand times in the length of a single light wave, and it is evident therefore that we cannot expect diffraction effects unless we can use light whose wave-length is

several thousand times shorter than that of visible light. In 1912, when v. Laue made his discovery, it was not known for certain whether X rays were electromagnetic waves, but it was known that if they were, their wave-length must be about ten thousand times shorter than that of visible light. Laue therefore suggested to Friedrich and Knipping that they should try the effect of passing a beam of X rays through a crystal, allowing the transmitted beam to fall on a photographic plate. It was to be expected that the diffracted beams, if present, would be very weak compared with the directly transmitted beam. A long exposure was therefore given, and, when the plate was developed, the central spot due to the direct beam was found to be surrounded by a pattern of spots, arranged in a manner corresponding to the symmetry of the crystal, and plainly due to diffracted beams. Upon this simple but brilliant experiment the whole subject of X-ray crystallography is based. We may sum up its results by saying that a crystal is to be regarded, in so far as its action upon X rays is concerned, as a 3-dimensional diffraction grating. It will be necessary therefore to consider briefly the problem of diffraction by such a grating, and it will be convenient to base our discussion upon the more familiar problems in one and two dimensions which occur in ordinary optics.

DIFFRACTION BY GRATINGS OF ONE, TWO AND THREE DIMENSIONS

Let us consider first of all the case of a screen perforated with a large number of small holes, $A_0, A_1, A_2, \dots$ (Fig. 5), equally spaced along a straight line. Upon this screen there falls a train of plane waves whose wave-length, λ , is of the same order as, but rather less than, the spacing, a , of the holes. Each hole, under the action of the incident waves, becomes the centre of a set of spherical wavelets spreading out on the far side of the screen. If the waves are incident normally on the screen, so that a given wave-front reaches all the

holes simultaneously, the corresponding spherical wavelets all start at the same instant. At any later time, therefore, they will all touch a cylinder, whose axis is the line of holes, which expands radially with the velocity of the waves, and this, by Huyghens' principle, is the resultant wave-front on the far side of the screen. There will of course be a cylindrical transmitted wave-front corresponding to each incident plane wave-front, the whole forming a train of cylindrical waves.

This wave train has the following important characteristic. The sum of the distances from any incident

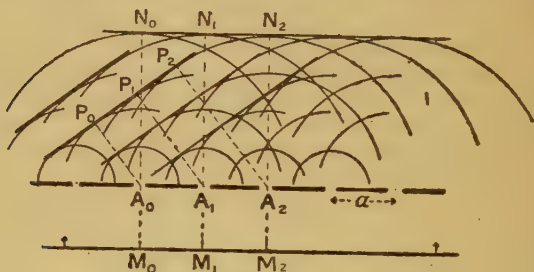


FIG. 5

Diffracted waves from a row of equally-spaced holes.

wave-front to a hole, and from the same hole to the cylindrical wave-front, is the same for all the holes. If $M_0M_1M_2 \dots$ is the trace of an incident wave-front, and $N_0N_1N_2 \dots$ the trace of one of the cylindrical wave-fronts in the plane of the diagram, $M_0A_0 + A_0N_0 = M_1A_1 + A_1N_1 = \dots$. In other words, the difference between the paths by way of any two holes from an incident to a transmitted wave-front is zero. A wave of this kind is called a wave of **zero order**. Owing to the equality of path, the wavelets from all the holes agree in phase on the transmitted wave-front; it is, in fact, this agreement which makes it a wave-front.

Now if, as we have supposed, the holes are equally

spaced, and if $a > \lambda$, it is easy to see that there will be other surfaces upon which the wavelets agree in phase, and hence, other transmitted waves. Imagine a conical surface, having $A_0A_1A_2$ as axis, of which $P_0P_1P_2 \dots$ is a trace, such that the path from the incident wave-front to it, by way of a hole, increases by one wave-length for each successive hole. Such a surface can be found if the holes are regularly spaced, but not otherwise. There will again be agreement of phase on this surface, for, if a crest of a wavelet from A_0 touches it, so will the crest emitted from A_1 one period earlier, and that emitted from A_2 two periods earlier, and so on. The conical surface is thus a possible wave-front, and we may call it the wave of the first order, since the path to it from any incident wave-front increases by *one* wave-length for each hole. In exactly the same way, other conical wave-fronts may be found for which the path difference from hole to hole is 2λ , 3λ , $\dots$ $n\lambda$, and these are called the waves of 2nd, 3rd, $\dots$ n th order. The greatest possible path difference for successive holes is a , so that n cannot be greater than a/λ . It will be seen that all the waves except that of zero order disappear if the spacing of the holes becomes irregular. It is only the regularity which makes it possible to find surfaces obeying the necessary conditions for *all the holes simultaneously*.

If the normal to the incident wave-fronts, instead of being perpendicular to the line of holes, makes an angle i with it, it will still be possible to construct the waves of the different orders. Suppose that the wave normal to the n th order wave makes an angle α with the line of holes. Let $M_0M_1 \dots$ (Fig. 6) be the trace of the incident wave, and $P_0P_1 \dots$ that of the n th order

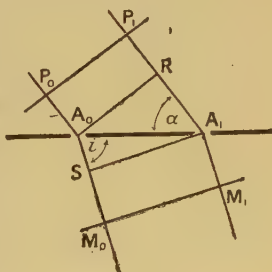


FIG. 6

wave. The path difference for successive holes is evidently $A_1R - A_0S$, or $a(\cos \alpha - \cos i)$. For the n th order wave we must therefore have

$$a(\cos \alpha - \cos i) = n\lambda \quad . \quad . \quad . \quad (2)$$

and, for a given value of i , we may obtain the different diffracted wave-fronts by putting $n = 0, 1, 2, 3, \dots -1, -2, -3, \dots$ in this equation. The wave of order n is a cone of semi-vertical angle $\pi/2 - \alpha$, and the locus of the possible directions of the wave normal from any hole to it is a cone of semi-vertical angle α , both cones having the line of holes as axis.

We may apply these results immediately to the case of holes arranged, in a 2-dimensional pattern, at the intersections of two sets of parallel lines with spacings a and b , so that any hole is a member of one row with a spacing a and of a second with a spacing b . Let the wave normal to the incident wave make angles i_1 and i_2 with the directions of the rows of spacing a and b respectively. Now, as we have seen, the wavelets from the holes of any row a will agree in phase on a surface normal to a direction making an angle α with the direction of a , which is given by

$$a(\cos \alpha - \cos i_1) = n_1\lambda \quad . \quad . \quad . \quad (3)$$

n_1 being a whole number, and, in the same way, all the wavelets from any row b will agree in phase on a surface whose normal makes an angle β with the direction of b , given by

$$b(\cos \beta - \cos i_2) = n_2\lambda \quad . \quad . \quad . \quad (4)$$

Now, for a given pair of values of n_1 and n_2 , there is one surface which satisfies these two conditions simultaneously, and that is the plane whose normal is defined by the angles α and β . Over this plane, the wavelets from all the holes in the pattern will agree in phase, and it is of course a diffracted wave-front. The possible diffracted waves from a 2-dimensional pattern are thus a series of diverging sets of plane waves, defined by the pairs of integers (n_1, n_2) , which may have any integral

values, positive, negative, or zero, which enable conditions (3) and (4) to be satisfied simultaneously.

To include the diffraction of X rays by a crystal, we must now extend this reasoning to three dimensions. The crystal units, presumably groups of atoms, are arranged at the points of a space-lattice. As an X-ray wave sweeps through the crystal, each atom scatters a small fraction of the radiation, and the crystal units thus become the centres of scattered wavelets between which a definite phase relationship holds, owing to the regular spacing of the crystal lattice, and the fact that all the wavelets are derived from the same incident wave. To express this fact, we say that the scattered radiation is 'coherent'. We have therefore exactly the generalization to three dimensions of the cases considered above.

Let a , b , c , be the spacings of the lattice in the directions of the three axes, that is to say the primitive translations. Let the incident wave normal make angles i_1 , i_2 , i_3 with the axes of a , b , and c respectively. A diffracted wave-front, whose normal is defined by α , β , γ , the angles which it makes with the three axes, will be formed if

$$\left. \begin{aligned} a (\cos \alpha - \cos i_1) &= n_1 \lambda \\ b (\cos \beta - \cos i_2) &= n_2 \lambda \\ c (\cos \gamma - \cos i_3) &= n_3 \lambda \end{aligned} \right\} \quad . \quad . \quad . \quad (5)$$

where n_1 , n_2 , n_3 , are whole numbers.

Now these conditions are far more stringent than those for diffraction at a 2-dimensional grating. For a given direction of incidence, i_1 , i_2 and i_3 are fixed. The first two conditions of (5) are satisfied, by certain values of α and β , and these fix the corresponding values of γ , since two angles are sufficient to fix the direction of a line. For a given wave-length, therefore, when the first two conditions are satisfied, all the quantities in the third equation are already fixed except n_3 , which must be a whole number. The three conditions cannot therefore in general be satisfied simultaneously except for

$n_1 = n_2 = n_3 = 0$, which gives a wave in the same direction as the incident wave, the wave of zero order. We therefore conclude that if a beam of X rays of given wave-length is passed through a crystal at any arbitrary angle of incidence there will not in general be any diffracted beams. It will be necessary to use certain angles of incidence, or, for a given angle of incidence, to vary the wave-length, and so to add another degree of freedom to the equations (5), before a diffracted beam is produced.

BRAGG'S RULE

Another way of regarding this stringency of condition was pointed out by W. L. Bragg, in his first paper on the subject in 1912, and is of great importance. As we have seen in Chapter I, the points of a space-lattice may be thought of as lying in a set of similar, equally spaced, parallel planes. Suppose a parallel beam of X rays is incident in a direction making a glancing angle θ with the surfaces of the planes. Each plane must be thought of as reflecting a very small fraction of the incident beam, for the process of combining the wavelets scattered by the crystal units lying in one plane is precisely the Huyghens construction for the reflexion of plane waves at a plane surface. Any diffracted beam which does occur must therefore be in a direction corresponding to reflexion of the incident beam from a set of crystal planes. There will, however, be no diffracted beam unless the waves reflected from the different planes are exactly in phase. If there is the smallest disagreement in phase between the beams reflected from successive planes, the regularity of the spacing of the planes, together with their huge number, will cause almost complete destructive interference. Now the path difference between reflected beams, derived from the same incident beam, and reflected at successive planes at a glancing angle θ , is easily seen from Fig. 7 to be $2d \sin \theta$, d being the spacing of the planes. Bragg's law may therefore be stated as follows. If a diffracted beam

is produced when a beam of X rays passes through a crystal, it must be in such a direction that it may be considered as derived by reflexion of the incident beam from one of the sets of lattice planes, but such a reflexion can only occur if the condition

$$2d \sin\theta = n\lambda \quad . \quad . \quad . \quad . \quad . \quad (6)$$

is satisfied, where θ is the glancing angle of incidence

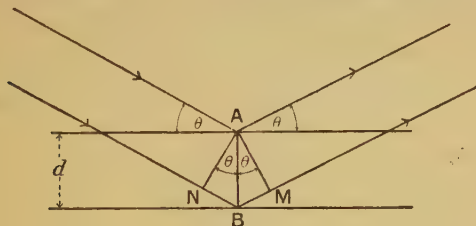


FIG. 7

Path difference between reflexions from successive planes.

The path difference = $NB + BM = 2d \sin\theta$.

of the X-ray beam on the planes in question and d is their spacing, n being an integer. This condition is of course mathematically equivalent to the conditions (5) given above: it provides, however, a very simple picture of the process of diffraction at a space-lattice, which is in practice nearly always thought of as reflexion at the lattice planes.

THE METHODS OF OBSERVING X-RAY DIFFRACTION SPECTRA

(1) **The Laue Method.** We have seen in the preceding section that if a beam of X rays of a given wavelength λ is passed in a given direction through a crystal, diffraction is not in general to be expected. We have also seen, however, that Friedrich and Knipping, on passing a beam of X rays through a slice of zinc blende, did in fact obtain diffraction. At first sight this result seems to contradict the theory, but a little consideration

will show that this is not so. The directions of the incident beam and of the crystal planes are fixed, and this fixes the directions of the possible diffracted beams, for they are obtained by supposing the incident beam to be reflected in the crystal planes. For each set of planes, the angle θ of the Bragg condition is thus fixed, and the only variables are n and λ . Now n has to be an integer, and if λ were fixed also it would only be a matter of chance if there were any diffracted beams. But, in the Laue method, an X-ray bulb with a platinum

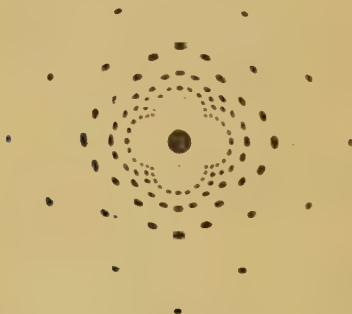


FIG. 8

The arrangement of the spots in a Laue photograph of a simple cubic crystal. X-Ray beam perpendicular to a cube face.

or tungsten target is used, which gives, in addition to the characteristic radiation, a continuous X-ray spectrum over a large range of wave-lengths: λ is therefore variable, and it will in general be possible to find values to satisfy the reflexion condition. Each spot on the Laue photograph is produced by a different wave-length, and if it were possible to obtain an optical Laue pattern, the spots would be differently coloured. Examination of the Laue photograph shows that the spots do actually occur at the positions to be expected from the reflexion law. The spots are seen to lie on a series of ellipses which pass through the central spot (see Fig. 8).

The spots on any one ellipse are produced by planes belonging to the same zone, that is to say, planes which are parallel to one common direction. Experimentally, the Laue method is comparatively easy. A narrow beam of X rays, limited by suitable lead slits, is allowed to pass through a slice of crystal, and then to fall normally on a photographic plate, wrapped in black paper and mounted in a convenient holder. The method has certain advantages, and, in skilful hands, has given valuable results, but the fact that the spectra are formed by different wave-lengths is a disadvantage and makes them difficult to interpret. We shall not consider the method in detail here.

(2) **The X-Ray Spectrometer.** The Laue method keeps the angle of incidence fixed, and alters the wave-length to satisfy the reflexion condition. Most other methods use X rays of a given wave-length, and alter the angle of incidence until the conditions are fulfilled. One of the earliest instruments using this method is the X-ray spectrometer, which was designed in 1913 by Sir William Bragg, and is founded very directly on the idea of reflexion at a set of crystal planes. Any face of a crystal is parallel to one of the sets of lattice planes. Suppose a beam of X rays of definite wave-length falls upon such a crystal face. There will in general be no reflected beam. If, however, the angle of incidence is adjusted to a value satisfying the reflexion condition, a reflected beam appears. The crystal, C in Fig. 9, is mounted on the table of a spectrometer, so that it can rotate about the axis of the instrument, the face from which reflexions are to be obtained being mounted so as to contain this axis. The collimator of the spectrometer is replaced by a system of slits, S_1 , which allow a narrow beam of X rays to fall upon the crystal face. The telescope of the spectrometer is represented by an ionisation chamber, I, which can rotate about the axis of the instrument, so as to receive any X-ray beam reflected from the crystal. The chamber has an aluminium foil window, and is provided with limiting slits

S_2 . It contains methyl bromide, or some other gas easily ionised by the X rays to be used. An insulated electrode E inside the chamber is connected to a sensitive electro-scope, the outer coating of the chamber being kept at a potential of several hundred volts by a battery of small accumulators. When a beam of X rays enters

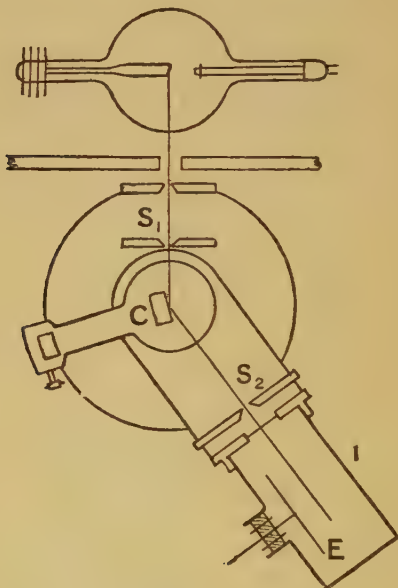


FIG. 9
The X-ray spectrometer.

the chamber, an ionisation current is set up, which is detected by the electro-scope.

An X-ray bulb with a molybdenum target is now generally used, which gives strongly the characteristic K radiation of the metal, consisting of two principal wave-lengths with only a comparatively faint continuous spectrum. The wave-lengths of the two chief lines, $K\alpha$

and $K\beta$, differ enough to be reflected at very different angles, so that, effectively, a monochromatic X-ray beam is being used. The wave-length of the $K\alpha$ group of Mo is about $0.710 \text{ \AA}$, which is a very suitable wave-length to give diffraction effects with spacings of a few Ångström units, such as occur in crystal lattices.¹

In using the instrument to find X-ray spectra, the observer varies the angle of incidence, θ , of the X-ray beam on the crystal face by slowly rotating the crystal table. The chamber is rotated at the same time at twice the rate of the crystal, so that it is always in the correct position to receive a beam of rays reflected from the crystal face. Reflexion will only occur for the values of θ which satisfy the equation $2d \sin\theta = n\lambda$. The settings of the crystal at which reflexion occurs are very sharp, and the angles $\theta_1, \theta_2, \theta_3 \dots$ corresponding to the different orders of reflexion can usually be determined to within a few minutes of arc, with ease.

The spectra may conveniently be denoted by the product of the Miller indices of the planes at which they are reflected and the order. Thus the first order from a (111) face would be called (111), the 3rd order (333), and so on. If the wave-length of the X rays is known, it is evident that the spacings of the planes can be determined from the spectrometer measurements. For example, with Mo $K\alpha$, (111) for the rock-salt crystal occurs at $\theta = 6^\circ 16'$, so that the spacing of the (111) planes is about $3.25 \text{ \AA}$. If the spacings of a crystal have been determined, using a known wave-length, the instrument can be used as a spectrometer for X rays, and unknown wave-lengths may be determined. The first measurements of the wave-lengths of X rays were made by Sir William Bragg with this instrument.

The spectrometer method has the great advantage that a quantitative estimate of the intensity of the reflexions can be made, which, as we shall see later, is of the greatest importance in determining crystal structures. Moreover, since the crystal is dealt with

¹ 1 Ångström unit = $1 \text{ \AA} = 10^{-8} \text{ cm}$.

face by face, the origin of the spectra is in all cases certain. On the other hand, a great deal of labour is necessary if a really representative set of spectra is to be obtained. It will be seen that to use the spectrometer to the best advantage it is necessary to have a fairly large crystal, with definite faces. If the required faces do not occur naturally, they may sometimes be ground or cut on the crystal in the proper directions, but it may frequently happen that no specimens of the crystal under investigation suitable for spectrometer work can be obtained. Some of the difficulties are avoided by the next method to be described.

(3) The Rotating-Crystal Method. Suppose a beam of X rays falls on a crystal so small that the incident beam is not completely absorbed. Reflexion can then take place at the planes within the crystal, if the necessary conditions are fulfilled, and a definitely developed external face is not necessary. For any arbitrary setting of the crystal it is unlikely that any set of planes will be in the correct position to reflect, but if the crystal is set into slow rotation about a fixed axis, a large number of planes will come successively into the reflecting positions, and the corresponding diffracted beams will flash out for a moment as the crystal passes through the correct setting, producing in the course of a number of rotations, upon a photographic plate set so as to receive them, a pattern of spots known as a rotation photograph. Two chief methods are used. In the first, the spots are received on a photographic film, bent into the form of a cylinder whose axis is the axis of rotation of the crystal. In the second, a photographic plate is placed at a distance of a few centimetres from the crystal, with its plane perpendicular to the incident beam. We shall consider the latter method in more detail.

Suppose the crystal to be mounted so that the c axis is parallel to the axis of rotation, to which the incident beam is perpendicular, and consider a spectrum which is formed in a direction making an angle ϕ with the

axis. By equation (3), such a spectrum cannot be formed unless $c \cos \phi = n\lambda$, c being the lattice spacing

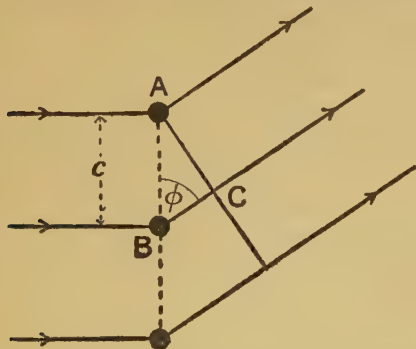


FIG. 10

The path difference between rays scattered from A and B is BC or $c \cos \phi$, and must be $n\lambda$ for a spectrum.

parallel to the c axis, and n a whole number (see Fig. 10). Any diffracted beams which do occur must there-

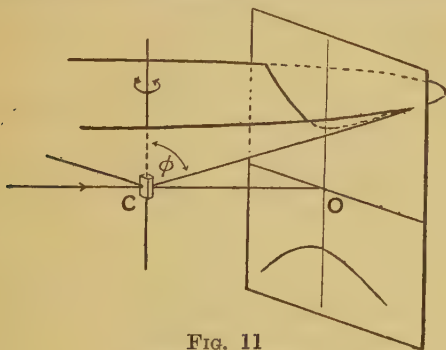


FIG. 11

The formation of layer-lines.

fore lie on the surfaces of a family of cones, whose axis is the axis of rotation, whose vertices are at the crystal

and whose semi-vertical angles, ϕ , are obtained by putting $n = 0, 1, 2, \dots -1, -2, \dots$ in the above relation. This family of cones will evidently intersect the photographic plate, which is parallel to its axis, in a series of hyperbolas (Fig. 11). The spots on the rotation photograph must therefore lie on this series of hyperbolas, which are known as layer lines, a translation of the German term *Schichtlinie*, and are denoted by the values of n to which they correspond. For $n = 0$,

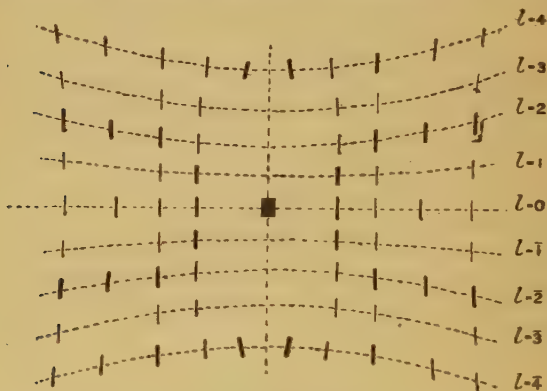


FIG. 12

The arrangement of the spots in a typical rotation photograph. (Hexagonal sodium sulphite, rotated through 30° about the c axis: radiation Mo K α .)

the cone becomes a plane containing the incident beam, and at right angles to the axis, intersecting the plate in a straight line.

If the crystal is such that the a and b directions are perpendicular to the c direction, which has been used as axis, the spots will lie at the intersections of the layer-lines with a set of curves transverse to them, which are known as row-lines. Examples of row-lines and layer-lines are shown in Fig. 12. Space does not permit of a discussion of the geometry of these lines, nor of the method of determining the indices of the spectra from

the positions of the spots on the rotation photograph : some of the results may, however, be stated without proof. If the index of a spectrum is denoted by (hkl) , and the rotation is about the c axis, all the spots on the zero layer-line will have $l = 0$, those on the first $l = 1$, those on the second $l = 2$, and so on. Further, all points on the same row-line have the same values of h and k . Thus (320) , (321) , (322) and (323) would all be on the same row-line.

The important point for the present discussion is that, from the spacing of the layer-lines, the lattice spacing in a direction parallel to the axis of rotation can at once be determined, for if the distance of the plate from the crystal is known, the distances of the layer-lines from the central spot, O , give at once the values of the angle ϕ , and hence, λ being known, the value of c . If rotation photographs are taken with rotations about all three axes separately, the spacings a , b and c , and hence, the size of the unit cell of the structure, are determined. The rotating crystal method is thus very powerful ; it gives the size of the unit cell, and a very large number of spectra with a large range of indices within the compass of three photographic plates. With a complete rotation, so many spots are in fact obtained upon a plate, that it is the usual practice to rotate the crystal backwards and forwards through an angular range of only about 30° in order to limit the spots on any one photograph to those of certain indices.

(4) **The Powdered-Crystal Method.** In many truly crystalline solids, individual crystals large enough even for the rotating-crystal method never occur. Such substances can, however, be examined by a method devised independently by Debye and Scherrer in Germany, and by Hull in America, in which a monochromatic X-ray beam is allowed to fall on a small specimen of the substance ground to a fine powder. The orientation of the minute crystal fragments being completely at random, a certain number of them will lie with any given set of lattice planes making exactly the correct

angle with the incident beam for reflexion to occur. Let θ be one such glancing angle of reflexion. The only necessary condition is that the planes should make an angle θ with the incident beam. Any fragment, there-

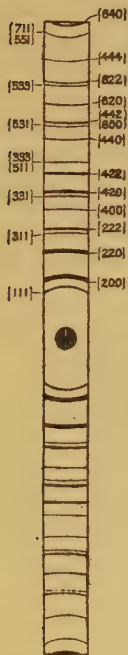


FIG. 13

Arrangement of
lines in a powder
photograph of NaCl.
Radiation CuK α , λ
= 1.54 Å.

fore, in which the normal to the plane in question makes an angle of $90 - \theta$ with the incident beam will be in a position to reflect, and since all orientations of the fragments are equally likely, the reflected rays will form a cone, whose axis is the direction of the incident beam, and whose semi-vertical angle is 2θ . For each set of planes, and for each order of spectrum, there is such a cone of diffracted rays: their intersections with a photographic plate set with its plane normal to the incident beam form a series of concentric circular haloes, from the radii of which the angles θ , and hence, the spacings of the planes can be deduced. It is generally necessary to obtain spectra for which the angle 2θ is more than a right angle, so that it is more usual to employ, instead of a plate, a cylindrical photographic film, nearly surrounding the crystal specimen. In one form of apparatus, the crystal powder is stuck, by means of gum, on a hair, which hangs vertically in the axis of a cylindrical camera, being stretched by means of a small weight. A photographic film fits round the inner surface of the camera, covering nearly the whole circumference. A narrow X-ray beam, suitably limited

by lead slits, falls on the powder, and afterwards passes out of the camera through a hole cut in the film, in order to minimize the fogging produced by the scattering of the direct beam. The intersections with the film of the cones of rays diffracted from the

powder produce a series of lines, each of which corresponds to a definite value of the glancing angle θ , and so, to a given spacing. A diagram of a typical powder photograph is shown in Fig. 13. In Fig. 14, P is the powder, O is the point where the direct beam would have struck the film, and A the point on the film, in a plane at right angles to the axis of the camera, and containing the incident beam, at which a spectrum with glancing angle θ is formed. If l is the distance from O to A, measured on the film, and R is the radius

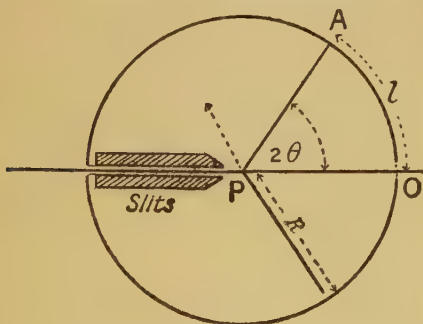


FIG. 14

The formation of a powder photograph.

of the camera, we have, from the figure, $\theta = l/2R$, so that by measuring l for the lines on the film the values of θ can be determined.

The powder photograph method is of great use in investigating the structures of simple crystals, particularly of those belonging to the cubic system, for which the spacings a , b , c , of the unit cell are all equal. For such crystals there are certain definite relationships between the angles at which spectra can occur, which makes the identification of the lines easy. Moreover, the spacings of all the planes parallel to faces of the same form $\{hkl\}$ are equal, and therefore produce spectra

at the same angle. For the most general case, in which h , k , and l are all different, there are 48 faces in the form, and 24 sets of planes all having the same spacing, and these all co-operate to produce one line on the film. Suppose now all the three axes are of different length, while still remaining at right angles to one another. The same general form $\{hkl\}$ now corresponds to six different spacings, and hence, to six different lines on the film. For crystals in which the axes are not at right angles, the multiplication of the lines is still greater, and the powder photograph becomes so complicated that identification of the lines is practically impossible. For the actual determination of structures, therefore, the powder method is of real value only for cubic, tetragonal, and hexagonal crystals. These types include, however, most of the metals and alloys, and a large number of simple binary compounds, the structures of which, owing to their habit of never crystallizing in large crystals, could not have been determined but for the powder method.

The powder photograph of a substance is characteristic of it, and can be used to identify it even if the crystal structure cannot be worked out. The powder method thus provides a powerful method of analysis and identification, and will doubtless be much used in this way in the future.

THE DETERMINATION OF THE STANDARD CRYSTAL SPACING

By using one of the methods described in the last section, it is possible to determine the unit cell of a crystal structure, that is to say the shape and dimensions of the units of pattern which, stacked together in countless millions, make up the crystal. Now, so far as we have gone at present, it appears not to be possible to determine the actual dimensions of the unit cell, but only its dimensions in terms of the wave-length of the X rays used in the investigation. This is of course true, so long as we confine ourselves solely to what may

be learnt from diffraction by the crystal lattice : nevertheless, in the case of very simple crystals, it is possible to determine the actual dimensions of the unit and so, the wave-length of the X rays. The first determinations of this kind were made in 1913 by Sir William Bragg,

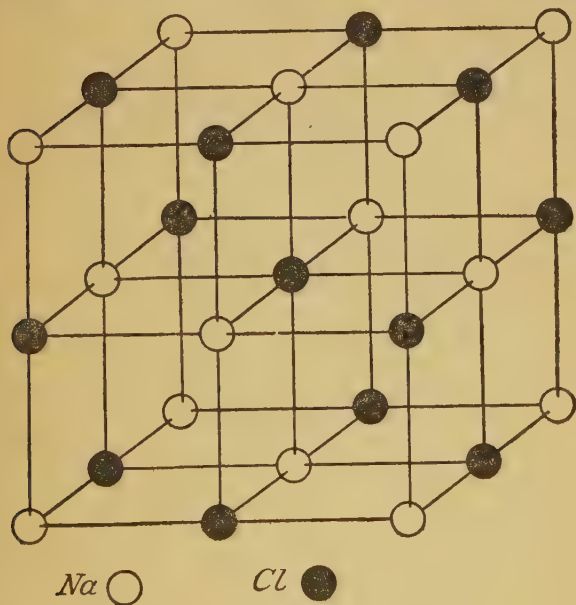


FIG. 15

The unit cell of the rock-salt structure.

using rock-salt and potassium chloride, in which the arrangement of the atoms had just been determined by W. L. Bragg. Each crystal has an exactly similar structure of the type shown in Fig. 15, and we will consider the case of rock-salt. The crystals are cubic, each atom being a member of three equally spaced rows at right angles to one another, the atoms of Na

and Cl always occurring alternately. Each Na atom has therefore 6 Cl atoms, and each Cl atom 6 Na atoms, as neighbours. The unit of structure which we obtain by starting, for example, with any Na atom, going along each axis in turn to the next Na atom, and completing the cube so defined, will be found to consist of a cube with a Na atom at each corner, and one in the middle of each face. The Na atoms, in other words, lie on a face-centred cubic lattice. So of course do the Cl atoms, their lattice being displaced half the edge of the unit cell along each axis with respect to the Na lattice.

Now such a unit cell contains four of each kind of atom,¹ and so four molecules of NaCl. Let M be the actual weight of a molecule of NaCl: the weight of the material in the unit cell is $4M$ gm. But if the length of the edge of the unit cell is a cm., and ρ is the density of the rock-salt crystal, the weight of the unit cube is ρa^3 gm. We therefore have $a^3 = 4M/\rho$, whence a can be calculated if M is known. Now, from the spectrometer measurements, the glancing angle θ at which the spectrum corresponding to the spacing a is formed is known, and we have, by Bragg's rule, $2a \sin \theta = \lambda$, whence, since we already know a , λ can be calculated.

The determination of the wave-length thus depends on a knowledge of M , the mass of the NaCl molecule, and so on the mass of the hydrogen atom, which in its turn, for its accurate determination, requires a knowledge of e , the charge on an electron. If we use Millikan's value of e , $4.774 \cdot 10^{-10}$ e.s.u., the length of the side of the unit cube of rock-salt comes out to be $5.628 \cdot 10^{-8}$ cm. at the ordinary temperature of the laboratory. All wave-length determinations based on diffraction by crystal lattices depend on this standard spacing, or on the corresponding one deduced from observations on calcite. The relative values of X-ray wave-lengths are known with considerable accuracy; the absolute values,

¹ Each atom at a cell corner is shared by eight cells, and so contributes $\frac{1}{8}$ atom to the unit, and each atom in a cell face is shared by two cells and so contributes $\frac{1}{2}$ an atom.

which are based on one of the standard lattice spacings depend on e , and would all be changed by a change in the accepted value of this constant.

It is evidently of great importance to obtain an independent check on the wave-length of X rays which shall depend only on direct measurements of length. Such a check has been made by Compton and Doan, who, using the fact that X rays are totally reflected at very small glancing angles from a smooth surface, and that the path differences for the successive elements of a reflexion grating become extremely small for glancing angles of a few minutes, were able to obtain optical diffraction of X rays from a ruled grating, and so to determine the wave-length directly, in terms of the measured grating space. The value obtained was in good agreement with that obtained from crystal measurements, and Compton's experiment is of the greatest importance on account of the check it gives of the general accuracy in principle of the methods used to obtain the true dimensions of crystal structures. It is of interest to notice that, if the attempts now being made to increase the accuracy of this direct method are successful, it will be possible to determine the value of e from crystal measurements, and it is probable that this will become the most accurate method.

In determining an unknown structure, the wave-length is taken as known, and the actual size of the unit cell is determined from the spacings of the layer-lines on rotation photographs, or otherwise. Then, from the density of the crystal, and its chemical composition, the number of molecules in the unit cell is calculated. This is only the first step: a complete determination of the structure involves finding the positions occupied by the individual atoms in the unit cell; but before considering how this may be done it will be necessary to return for a time to the purely geometrical aspect of the subject, and in continuation of the matters discussed in Chapter I, to take up the study of crystal symmetry.

CHAPTER III

THE SYMMETRY OF CRYSTALS AND ITS DETERMINATION BY MEANS OF X RAYS

EXTERNAL SYMMETRY

STUDY of the external forms of crystals reveals the fact that most of them possess geometrical symmetry. A geometrical figure is said to possess symmetry if, by performing on it some geometrical operation, such as rotation about an axis, or reflexion across a plane, it can be brought into self-coincidence. For example, a square can be brought into self-coincidence by rotating it through a right angle about an axis perpendicular to its plane, and passing through its centre, or by reflecting it across a plane passing through its centre and perpendicular to its sides, and in a number of other ways. In studying the symmetry of crystals, we consider not the actual form of any real crystal, which will depend on the accidents of growth, but the radiating bundle of normals to its faces from some internal fixed point, or the points where these normals cut a sphere whose centre is their origin, which, as we have seen in Chapter I, are the true representations of the geometrical form of the crystal.

It is found as a matter of observation that, so far as the external forms of crystals are concerned, the following elements of symmetry may occur :

(a) **2-fold, 3-fold, 4-fold or 6-fold (but not 5-fold) rotation-axes of symmetry.** A figure is said to possess an n -fold rotation axis of symmetry if it is brought into self-coincidence by a rotation of $2\pi/n$

about that axis. The symmetry axis of the square mentioned above is a 4-fold axis. These axes are also called digonal, trigonal, tetragonal and hexagonal axes.

(b) **Centres of Symmetry.** If a figure has a centre of symmetry, O , then to every point A of the figure there corresponds a point A' such that AOA' is a straight line, and $OA = OA'$.

(c) **Reflexion Planes of Symmetry.** A figure has a reflexion plane of symmetry if by reflexion in that plane, as in a mirror, but in both directions, the figure is brought into self-coincidence.

(d) **4-fold and 6-fold Alternating Axes, or Rotation-Reflexion Axes.** The operation of an n -fold alternating axis consists of a rotation through $2\pi/n$ about the axis, followed by a reflexion across a plane at right angles to the axis. n must evidently be even, and a 2-fold alternating axis is equivalent to a centre of symmetry, so that $n = 4$ and $n = 6$ are the only possibilities. A rhomb of calcite has, for example, a 6-fold alternating axis.

The geometrical forms of crystals may be classified according to their possession of one or more of the symmetry elements enumerated above. Since we are dealing with the symmetry of a set of normals radiating from a point, it follows that any symmetry planes or axes concerned must go through this point. We have therefore a perfectly definite geometrical problem. What combinations of the above symmetry elements are possible, subject to the conditions that all of them pass through a single point? A group of symmetry elements of this kind is known as a **Point Group**. It is found that 32 such groups are possible, so that there should be 32 possible classes of crystal, arranged according to the symmetry of their external forms. These 32 classes do in fact include all the known types of crystal symmetry, and, with a few doubtful exceptions, examples of every class are known.

CRYSTAL SYSTEMS

The crystal classes may be divided into seven main **Systems**, each characterized by the possession of a certain minimum of symmetry elements, and referable to certain characteristic axes. The systems are :

(1) **Triclinic**, possessing no symmetry at all, or at the most, a symmetry centre. In the first case opposite faces will have different properties, in the second, the same properties. Referable to 3 unequal axes, not at right angles.

(2) **Monoclinic**, possessing a single 2-fold axis, or a single reflexion plane. Referable to 3 unequal axes, one at right angles to the other two.

(3) **Orthorhombic**, having two symmetry planes at right angles, or three 2-fold axes at right angles to one another. The existence of two such axes demands the existence of a third. Referable to 3 unequal axes at right angles.

(4) **Trigonal**, having a single 3-fold axis. Referable to 3 equal axes equally inclined to the 3-fold axis.

(5) **Tetragonal**, having a single 4-fold axis, simple or alternating. Referable to 3 axes at right angles, two of them equal.

(6) **Hexagonal**, having a single 6-fold axis, simple or alternating. Referable to two equal axes inclined at 120° and a third, unequal axis at right angles to them.

(7) **Cubic or Regular**, having four 3-fold axes, corresponding in direction to the diagonals of a cube. Referable to 3 equal axes at right angles to one another.

The symmetry elements given above are in each case the minimum required to place the crystal in the system in question; they are not, however, in general incompatible with the existence of other symmetry elements at the same time, and in fact the existence of two symmetry elements in general conditions the existence of others. For example, two 2-fold axes at right angles demand a third at right angles to both (Fig. 16b).

Adding a symmetry centre to these also adds three reflexion planes at right angles to one another, and the group has now the highest symmetry of the orthorhombic system (Fig. 16c). Starting in this way with the lowest symmetry requirements of each system, we may add one by one the compatible symmetry elements, until the highest possible symmetry of the system has been reached. This procedure gives in all 32 point-groups of symmetry elements, corresponding to the 32 crystal classes. The three point-groups of the orthorhombic system are shown in Fig. 16.

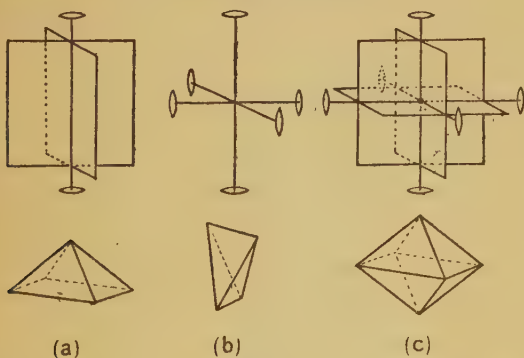


FIG. 16

The three point-groups of the orthorhombic system with their corresponding geometrical forms.

- (a) Di-digonal polar (Miers). Two reflexion planes at right angles and a 2-fold axis.
- (b) Digonal holoaxial. Three 2-fold axes at right angles.
- (c) Di-digonal equatorial. Three 2-fold axes, three reflexion planes and a centre of symmetry.

If a crystal belongs to a particular class, it must possess, corresponding to any one face, all the other faces which can be derived from the first by the symmetry operations belonging to the class. The faces will not of course as a rule be equally well developed on any particular crystal. The class having the highest possible symmetry for a system is called the **holohedral** class of that system. Classes having less than the full

symmetry are called **hemihedral** or **tetartohedral** (having half or a quarter of the complete set of faces).

It is quite usual, however, to refer to any class having less than the full symmetry of its system as hemihedral.

A regular tetrahedron, for example, has hemihedral cubic symmetry. It has the four 3-fold axes characteristic of that system, but it has only six of the nine possible reflexion planes, the three 4-fold axes have become 4-fold alternating axes, and the six 2-fold axes, and the symmetry centre have vanished.

THE SYMMETRY OF SPACE-LATTICES

We must now consider how far the observed symmetry properties of crystals are in harmony with the idea of the crystal as founded on a space-lattice. In studying the symmetry of space-lattices, it is essential to realize that we are no longer dealing with axes and planes of symmetry all of which pass through a single point. If an element of symmetry passes through any point of one cell of a lattice, a precisely similar element must pass through the corresponding points of every cell of the lattice, for the cells are all exactly similar, and not to be distinguished from each other in any way. Each one of these symmetry elements must, moreover, bring the whole lattice, including all the other symmetry elements, into self-coincidence, and only those symmetry elements, and their combinations, which are consistent with these requirements are possible. A little consideration will show that this explains the absence of 5-fold axes, for it is not possible to arrange such axes in this way.

Bravais showed, many years ago, that there are 14 possible types of space-lattice. Of these, one is triclinic, two are monoclinic, four orthorhombic, two tetragonal, two hexagonal and three cubic. The classification of the lattices refers to their symmetry as a whole, and not to that of their true unit cells. This will be clearer from the consideration of an example, and we shall take the case of the three cubic lattices.

The simplest cubic lattice is that in which the lattice points lie at the corners of cubes. The three primitive translations are all equal, and at right angles, and this is the true cubic space-lattice. The other cubic lattices are the face-centred cube, which we have already met with in the case of NaCl, having a point at each corner of a cube and one in the middle of each face; and the

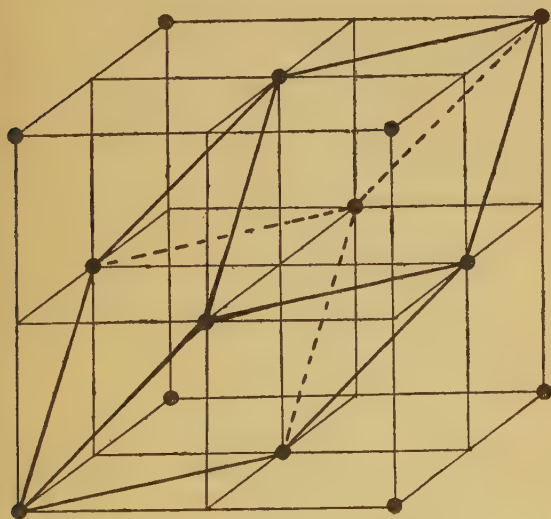


FIG. 17

The true unit cell of the face-centred cubic lattice.

body-centred cube, having a point at each cube corner and one at the cube centre. These lattices are classed as cubic because they have full cubic symmetry; they are not, however, cubic space-lattices in the sense that their primitive translations are at right angles. If, in the face-centred lattice shown in Fig. 17, for example, we start from any point of the lattice and take three axes at right angles, we can never include more than

the points at the cube corners. Those at the face centres, or three-quarters of the total number of points are left out. The face-centred cube is, however, a true space-lattice, although not a cubic one. If we start at a cube corner and draw lines to the three nearest face centres of the same cube, we may take these lines as the primitive translations of a rhombohedral lattice which will include all the points. Its unit cell, which is outlined in Fig. 17, has one-quarter of the volume of the cube. The face-centred lattice is thus a special case of a rhombohedral, or hexagonal, lattice, which happens to possess cubic symmetry, and in a similar way it can be shown that the body-centred lattice is a special case of a monoclinic lattice. Similar considerations apply to lattices belonging to the other systems.

Each of the 14 types of space-lattice has the fullest possible, or holohedral, symmetry of its system, and thus, so far as space-lattice symmetry alone is concerned, there are only six types of symmetry, not even seven, since there is no trigonal lattice. Now we have seen that crystals of 32 classes of external symmetry are known, and it follows, therefore, that considerations other than the symmetry of the fundamental space-lattice must come in in determining the actual symmetry of a crystal. Bravais recognized this, and pointed out that the symmetry of the whole structure would be reduced if the crystal-unit associated with the lattice point had a symmetry lower than that of the lattice as a whole. In deducing the possible symmetry of space-lattices, the assumption is made that the lattice points are mathematical points, and are completely symmetrical: if we replace the mathematical point by a geometrical figure, or by a collection of points, the symmetry of the whole lattice cannot be higher than that of the figure, or group of points. In this way Bravais explained the phenomenon of hemihedrism. It was only necessary to ascribe to the lattice units the symmetries of the various crystal classes to account for all the observed types of crystal symmetry.

THE SPACE-GROUP

For the X-ray crystallographer, the Bravais unit becomes a group of atoms in the unit cell, and if, for the time being, we can treat each atom as having spherical symmetry, or as a point, the geometrical problem which arises may be stated as follows. What types of symmetry are possible for a collection of exactly similar groups of points, each group being associated with one of the points of a Bravais lattice, and derived from any other group by the translations of the lattice? Fortunately for the rapid development of the subject, the answer to this purely geometrical question was already known at the time when the diffraction of X rays was discovered, owing mainly to the work of Sohncke, Fedorow, Schoenflies and Barlow.

The problem is that of combining symmetry elements into a space pattern. We have seen that, if a symmetry element passes through any point in one lattice cell, a similar element must pass through the corresponding point in every other cell. The existence of the symmetry elements in general demands the existence of others, and other additional symmetry elements may be combined with those already present, again in the same way in each unit cell; but any possible symmetry element must always be such as to bring, by its operation, the whole group of symmetry elements into self-coincidence. The assumption is of course made all through that the groups are of infinite extent. Each such possible group of symmetry elements is called a **Space-Group**, and their total number is found to be 230. It is very important to realize that a space-group is a group, or scaffolding, of symmetry elements, and not a group of points. If a geometrical point is placed anywhere in such a group, it is multiplied by the action of the symmetry elements into a collection of points associated with a lattice cell, and, by the translations of the lattice, into a similar collection of points associated with each cell, that is to say, into a pattern in space. An infinite

number of different patterns could be produced according to the exact position of the original point, but all would have the same symmetry elements, and would belong to the same space-group.

We shall consider a 2-dimensional example. Suppose that Fig. 18 represents part of an infinite rectangular network, at each point A of which is a 2-fold rotation axis, perpendicular to the plane of the net. Remembering that the pattern is supposed to extend indefinitely in all directions in the plane, we see that each of the

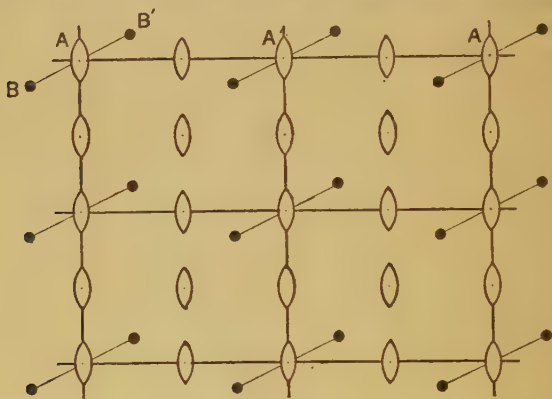


FIG. 18

Arrangement of 2-fold rotation axes, denoted by $\odot$, perpendicular to a rectangular network.

2-fold axes by its action, a rotation through 180° , brings the whole set of axes into self-coincidence. If a point B is placed near one of the axes, it is turned by the axis into B', and the translations of the lattice then produce exactly similar pairs of points about each A axis. It will now be seen from the figure that there are, in addition to the A axes, other sets of 2-fold axes in the middle of each rectangle of the net, and at the mid-point of each side, half-way between the A axes. The existence of the A axes necessitates the existence

of these other axes, and the action of the whole group of symmetry elements on the single point B produces the pattern. Other independent points could of course be put in, and the complexity of the pattern increased. Any set of points derived by symmetry from the same point are said to be **equivalent**.

GLIDE PLANES AND SCREW AXES

Certain symmetry elements are possible in an extended group which are not possible in a point group. These are glide planes and screw axes. The nature of a glide

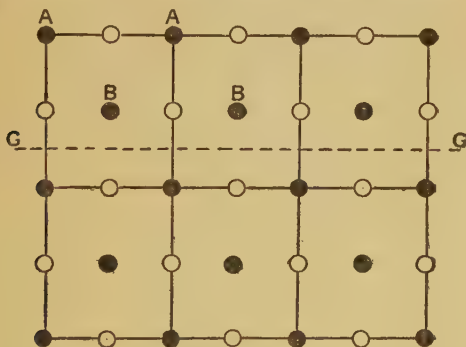


FIG. 19

Illustrating glide planes of symmetry.

plane may be understood from Fig. 19. The black circles B lie at the midpoints of the rectangles formed by the black circles A, all the circles A and B being alike. Let GG' be the trace of a plane, perpendicular to the plane of the paper, and half-way between the lines of circles A and B. By reflexion across this plane, the black circles are brought to the positions shown by the white circles in the diagram, and if these are given a translation, parallel to the plane of reflexion, of one-half the spacing AA , they coincide again with the original A and B circles. The whole figure is, in effect,

brought into coincidence by a reflexion across GG' and a translation of half the lattice spacing parallel to the plane of reflexion. If now we imagine the figure extended to three dimensions, so that a set of points similar to A lie at equal intervals exactly below them, the B points being supposed to lie in planes half-way between the A planes, the figure can again be brought into self-coincidence by a reflexion across GG' and a glide, parallel to the plane, of half the A spacing in the plane of the paper plus half the A spacing in a direction perpendicular to the plane of the paper. These examples illustrate the two types of glide plane.

An n -fold screw axis produces a rotation of $2\pi/n$ about the axis and a translation parallel to the axis whose amount depends on n . If, in Fig. 19, we now take GG' as an axis, instead of as a trace of a plane, we see that a rotation of 180° about GG' , together with a translation of $\frac{1}{2}AA$ parallel to the axis, brings the figure into self-coincidence. The translation for a 2-fold screw axis is always half the spacing of the lattice in the direction of the axis; for a 3-fold axis it is $\frac{1}{3}$, and, in the simplest cases, for the 4-fold and 6-fold axes, $\frac{1}{4}$ and $\frac{1}{6}$ of the spacing respectively. In all these cases except that of the 2-fold axis, the equivalent points are arranged spirally about the axes, and we have to distinguish between right- and left-handed rotations. For a 4-fold axis a translation of $\frac{1}{2}$ is also possible, this axis giving an arrangement of equivalent points which has also a 2-fold rotation axis. A 6-fold screw axis with a translation of $\frac{1}{3}$ may be either right- or left-handed, and the resulting arrangements of points have at the same time a 2-fold rotation axis and a 3-fold screw axis, while a translation of $\frac{1}{2}$ gives a set of points having a 3-fold rotation axis and a 2-fold screw axis.

The addition of these new kinds of symmetry element, and the fact that, in a space-group, the planes and axes do not all pass through one point, greatly increases the number of combinations of symmetry elements which are possible, and we need not be surprised that the number

of groups has increased from 32, for the external form alone, to 230 when the inner structure is taken into account. If we take as an example the class of the orthorhombic system having three 2-fold axes, we shall find that, instead of the one possibility for the point group, there are nine ways, which are illustrated in Fig. 20, of combining three such axes, including of course screw axes. These all correspond to one crystal class, or, in other words, to one type of external symmetry.

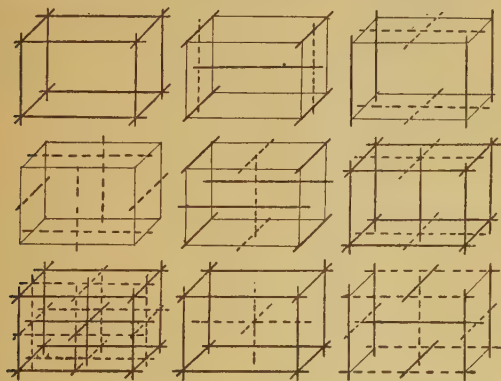


FIG. 20

The nine space-groups of the orthorhombic holoaxial class (three 2-fold axes at right angles, cf. Fig. 16b). Each parallelepiped is $\frac{1}{8}$ of the corresponding unit cell. Rotation axes denoted by thick continuous lines, screw axes by dotted lines.

If we add a centre of symmetry to the axes, so as to produce the holohedral class of the system, we find that there are 28 possible combinations of axes and symmetry centres, or 28 holohedral orthorhombic space-groups. There are, in all, 60 space-groups in the orthorhombic system, corresponding to only three point groups, or classes of external symmetry.

THE COMPOUND SPACE-LATTICE

Before we proceed to discuss the determination of the space-lattice and the space-group, a little further

geometrical preparation is necessary. We suppose the crystal to consist of exactly similar groups of atoms, indistinguishable either in themselves or in their surroundings, and therefore associated with the points of a space-lattice. Now each atom in the unit of structure must lie on its own space-lattice, which is equal and parallel to the lattice upon which the whole structure is based ; for each atom in a given unit is to be derived from the corresponding atom in any other unit simply by the translations of this lattice. We have therefore the following important result. **A crystal structure having N atoms in the unit cell may be regarded as consisting of N equal and parallel inter-penetrating space-lattices, one for each atom of the unit.** Now we have seen that the atoms of any one space-lattice may be considered as lying on sets of equally spaced and identical planes. To each of the lattices of which, as we have just seen, we may suppose a structure to be built up there will correspond sets of planes. The planes characterized by given indices (hkl) will be parallel for all the lattices, but they will not in general coincide, and, instead of a single set of exactly equal planes repeating at a definite interval d , there will be identical groups of N planes repeating in the same interval. Since all the lattices are alike, each plane of a group will have the same number of atoms per unit area, the atoms on any one plane being all of one kind. It may happen that some of the planes of the group will coincide, but, in general, there will be one for each atom of the unit. The matters discussed in this paragraph are illustrated in two dimensions in Fig. 21, in which the space-lattices are represented by net-planes and the lattice planes by rows of points.

THE REFLEXION OF X RAYS BY A COMPOUND LATTICE

We must now consider the reflexion of X rays from a compound lattice such as that discussed in the last section, in which the single planes of the simple lattice are replaced by groups of planes. The angles at which

the spectra are formed are just the same as for the simple lattice, since they depend only on the interval in which the pattern repeats itself, which may conveniently be termed the **identity period** for the set of planes. If, at any angle, the reflexions from the planes of atoms of one kind, A say, in successive groups of planes are in phase with one another, so are those from

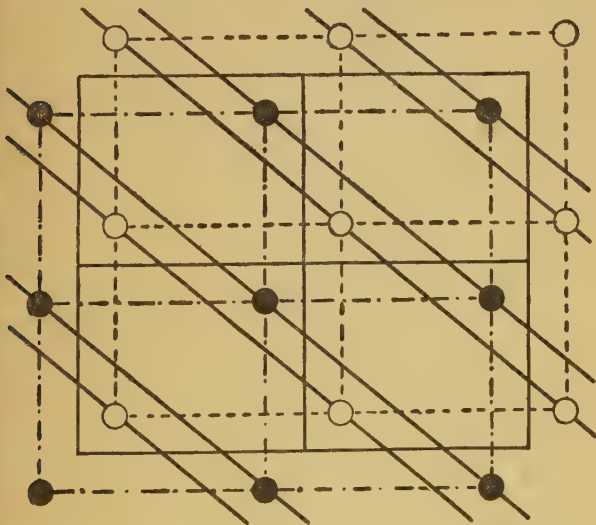


FIG. 21

Two-dimensional compound lattice.

Each kind of point lies on its own 2-dimensional lattice. The rows of points occur in pairs, one row for each kind of point.

the planes of atoms of another kind B, and so on for all the N kinds of plane. The reflexions from the different planes belonging to the *same* group will not, however, in general be in phase, so that the total amplitude reflected from the group will be less than it would have been had all the planes been coincident.

Suppose, for example, that the group consists of two

planes only, one of kind A, the other of kind B. Let d be the spacing between successive planes of the same kind, or the identity period of the lattice in the direction concerned, and let x be the distance between the A and B planes of the same group. For a first order reflexion, the phase difference corresponding to a distance d is 2π , for there is a path difference of λ between the beams reflected from successive planes of the same kind. The phase difference between the beams reflected from a plane A and a plane B at a distance x apart is therefore $2\pi x/d$ for the first order, and $2\pi mx/d$ for the m th order. If the B planes are exactly half-way between the A planes, so that $x = d/2$, the phase difference for the m th order becomes $m\pi$. In this case, for the spectra of even order, the reflexions from the planes A and B are exactly in phase, while, for the spectra of odd order, they are exactly out of phase. If the A and B planes had been coincident, so that the reflexions from them were in phase for all orders of spectra, the latter, as we shall see later, would have fallen away regularly in intensity as the order increased. We may call such a set of spectra a **normal** series. With the B planes half-way between the A planes, we see that the spectra will be alternately weaker than and equal to those of the normal series. This case is realized by the (111) planes of NaCl, which consist of alternate sheets of Na and Cl atoms, and the spectra from these planes do in fact show this alternation in intensity. If the atoms A and B had been of the same kind, the odd orders of spectra would have been entirely absent, for in this case planes of the same kind would repeat at intervals $d/2$, instead of d , and the first order from planes with a spacing $d/2$ will of course occur at the same angle as the second order from planes with spacing d .

We see, then, that the interval in which the pattern repeats itself, or the identity period of the structure, determines the angles at which the spectra occur, but that the distribution of the atoms in the unit cell, which determines the spacing of the planes of the

individual groups, controls the intensities of the spectra. It is by studying the intensities, therefore, that we may hope to determine the actual arrangement of the atoms.

CALCULATION OF THE PHASE DIFFERENCES

We shall now show how it is possible to calculate the phase differences between the reflexions from the planes of the different constituent lattices. Consider a simple space-lattice whose translations are a , b , c , and let one of the lattice points be taken as the origin of co-ordinate axes, x , y , z , which lie in the directions of a , b , c , respectively. We shall assume here that the axes are at right angles, since this simplifies the geometry; the necessary modifications for oblique axes are quite easy to make.

The perpendicular distance from a point whose co-ordinates referred to the axes are (x, y, z) to a plane through the origin, the direction cosines of whose normal are λ , μ , and ν is $\lambda x + \mu y + \nu z$. Now we have seen in Chapter I that the direction cosines of the normal to a plane whose indices are (hkl) , in a lattice with translations a , b , c , are proportional to h/a , k/b , l/c . Moreover, for rectangular axes, the sum of the squares of the direction cosines must be unity (there is a more complicated relationship for oblique axes), and this enables the actual direction cosines to be calculated. They are in fact the numbers h/a , k/b , l/c , each divided by the quantity $\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}$. Let us denote the quantity beneath the square-root sign by $1/D^2$.

The general co-ordinates of a lattice point are (ma, nb, pc) , where m , n and p are integers, positive, negative or zero. The perpendicular distance from this lattice point to the plane (hkl) passing through the origin is therefore $D\left(\frac{h}{a}ma + \frac{k}{b}nb + \frac{l}{c}pc\right)$ or $D(mh + nk + pl)$

Now through each lattice point (ma, nb, pc) there passes a plane (hkl) , and the perpendicular distance we have calculated is the distance between this plane and the corresponding plane through the origin. The **spacing**,

or identity period, of the (hkl) planes is the distance between successive (hkl) planes, and is therefore the least value of $D(mh + nk + pl)$, exclusive of zero. Now, since h, k, l, m, n, p , are integers, and since m, n, p , may have any positive or negative values including zero, the smallest value of $(mh + nk + pl)$ which is not zero is evidently unity. Thus the spacing of the (hkl) planes for the simple orthorhombic lattice (a, b, c) is D , or $(h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2}$. For a cubic lattice, for which $a = b = c$, D becomes $a/\sqrt{(h^2 + k^2 + l^2)}$.

Suppose, now, that the unit of structure consists of a group of N atoms, $A, B, C, \dots$, which we shall suppose associated with each point of the lattice considered in the last paragraph. As before, we take axes parallel to the lattice translations, and choose a convenient origin, which may or may not contain an atom. Let (x, y, z) be the co-ordinates of some atom in the unit. A plane (hkl) passes through this atom, and through the corresponding atoms in certain other units, and this is one of the N planes of the composite (hkl) group corresponding to the complex unit of structure. A beam of X rays is supposed reflected in turn from the plane (hkl) passing through the point (x, y, z) and from the parallel plane through the origin. Let us calculate the phase difference, ϕ , between the two reflected wave-trains when both contribute to the m th order spectrum from the (hkl) planes of the compound lattice. The distance between the two planes is the perpendicular distance from the point (x, y, z) on to the plane (hkl) through the origin, which, as we have already seen, is $D(hx/a + ky/b + lz/c)$. Since the spacing D corresponds to a phase difference of $2m\pi$ in the m th order spectrum, the phase difference, ϕ , between the wave-trains reflected from the plane through the point (x, y, z) and that through the origin is given by

$$\begin{aligned}\phi &= 2\pi m(hx/a + ky/b + lz/c) \\ &= 2\pi (mh.u + mk.v + ml.w) \quad \dots \quad (7)\end{aligned}$$

where (u, v, w) are the co-ordinates of the atom (x, y, z) ,

expressed as fractions of the corresponding sides of the unit cell of the lattice. This important expression for the phase is quite general, and applies equally to oblique axes. It enables us at once, if we know the co-ordinates of the atoms in the unit, to write down the relative phases of their contributions to any spectrum. In practice, it is usual to denote a spectrum by (hkl) , the indices being then understood to be the Miller indices multiplied by the order, or the numbers mh , mk , ml , in equation (7). In what follows, we shall adopt this convention.

THE STRUCTURE-AMPLITUDE

For each of the N atoms in the unit of structure, there will be a corresponding (hkl) plane, the phase for a reflexion from which can be calculated, in the way just described, from the co-ordinates of the atom, which we will suppose known. The problem now to be solved is to find the resultant amplitude of the wave reflected from the complex of N planes. The relative phases are known, and if we know the amplitude of the wave reflected from each plane, the resultant amplitude can be written down at once from the usual formula for combining simple harmonic waves having the same frequency but different amplitudes and phases. This resultant amplitude, it will be remembered, is given by the length of the side closing a polygon whose other sides are equal in length to the amplitudes of the waves whose resultant is required, the side representing any one component wave making an angle with some fixed direction equal to the phase of that component. Let the amplitude scattered by the planes of atoms of the kind A alone in the direction considered be denoted by A , that by planes of the kind B by B , and so on. Let the phases for the reflexions from the different planes, calculated from (7), be ϕ_A , ϕ_B , . . . Then, if S is the resultant amplitude scattered in the direction of the (hkl) spectrum, the phase-amplitude polygon gives at once

$$S^2 = (A \cos \phi_A + B \cos \phi_B + \dots)^2 + (A \sin \phi_A + B \sin \phi_B + \dots)^2 \quad (8)$$

The quantity S is called the **structure-amplitude**. It is a measure of the amplitude reflected from one of the complex groups of N planes in the direction of the (hkl) spectrum. The groups repeat at intervals D and, in the directions of the spectra, the contributions of all the groups are in phase, so that the total amplitude reflected by all the planes will be proportional to S , and the intensity to S^2 .¹

If the crystal has a symmetry centre, and if this is chosen as origin, the atoms occur in pairs, for every atom with a given phase ϕ there is a corresponding atom with a phase $-\phi$; the sine terms in the expression for S^2 vanish, and we are left with

$$S = 2A \cos \phi_A + 2B \cos \phi_B + \dots \quad (9)$$

It is often possible to use the expression in this form, but it must always be remembered that this implies the existence of a symmetry centre, and its choice as origin. If the crystal has no symmetry centre, or if some other point is chosen as origin, the full expression for S must be used.

The quantities $A, B, \dots$ in equations (8) and (9) are evidently proportional to the average amplitude scattered by single atoms of the kinds considered in the direction of the spectrum. If the relative scattering powers of the atoms and their positions in the unit cell are known, we can calculate S , and hence the amplitude of the (hkl) spectrum, in terms of the amplitude which it would have had, had all the atoms in the unit been concentrated in a single plane. Conversely, if we

¹ It should be noticed that the assumption that the total reflected intensity is proportional to S^2 is equivalent to the assumption that the contribution to the total amplitude from each atomic plane is unaffected by the presence of the other planes. The radiation reflected by one set of planes is scattered to some extent by the others before emerging from the crystal. This effect, which is most marked for intense reflexions, modifies the formula for the reflected intensity, but not, of course, the amplitude reflected from a single group of planes corresponding to a crystal unit.

measure the relative intensities of the different spectra, we may, by examining the way in which they vary, be able to determine the co-ordinates of the atoms. All methods for determining the structures of complex crystals are based on this idea.

DETERMINATION OF THE SPACE-LATTICE

We shall now apply the formulæ developed in the preceding section to the determination of the space-lattice upon which a structure is built. Suppose, for example, that we are investigating a crystal of orthorhombic or cubic symmetry, and that we have already determined the size of the unit cell. We shall naturally have chosen orthorhombic or cubic axes, but as we have already seen on page 39, it does not follow that the translations of the true space-lattice are parallel to these axes. It is easiest to consider a special case, and we shall take the body-centred cubic lattice, consisting of a point at each corner of a cube and one at the centre. Whatever the structure of the crystal may be, similar groups of atoms are associated with each of the lattice points, and, for our present purpose, we may simply assume that at each cube corner and centre there is a similar scattering unit. The crystal is cubic, and we shall have chosen cubic axes. From this point of view, the lattice must be considered as two interpenetrating simple cubic lattices, the corners of one lying at the centres of the other (Fig. 22). The lattice can be thought of as consisting of two similar scattering units associated with each point of a simple cubic lattice. Let us express the co-ordinates of these two units as fractions of the lattice spacings, and work out the structure amplitude in the way described above. We take one point of the lattice as origin; its co-ordinates are then (000), the co-ordinates of the second point which lies at the centre of the cell are then $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, expressed as fraction of the lattice spacings. The phases for the (hkl) planes corresponding to the two scattering units are

then, by (7), 0 and $(h + k + l) \pi$. The expression for S therefore becomes, by (8),

$$S = R \{1 + \cos (h + k + l) \pi\},$$

R being the amplitude scattered by a single lattice unit. Now S vanishes whenever $(h + k + l)$ is odd. The intensities of all spectra for which (hkl) satisfy this condition are therefore zero.

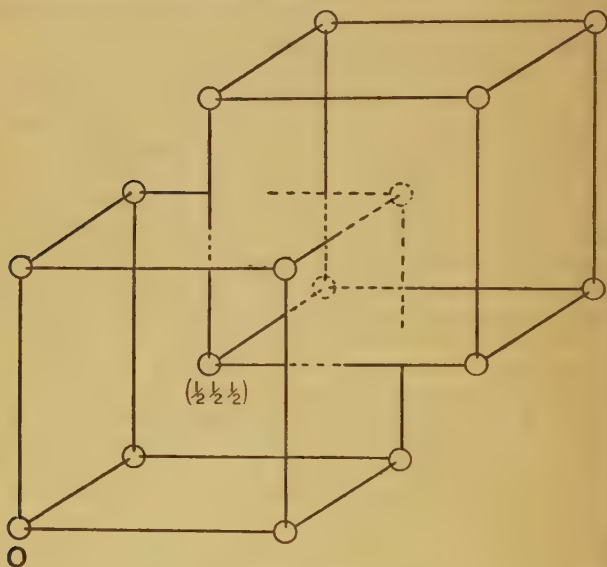


FIG. 22

Body-centred cubic lattice.

Let us consider a little more carefully what this means. We have taken cubic axes, and have determined the distances parallel to these three axes in which the structure repeats itself, these of course being all equal in this case. This gives a cubic unit cell and, on this, the spacings, and the indices (hkl) of the spectra are based. If the cell is also the true space-lattice cell

of the structure, spectra representing all values of (hkl) should appear. If the lattice is body-centred, we must associate with each unit of the simple lattice a second similar unit lying at the centre of the cell. The presence of this second unit in this very special position causes certain systematic vanishings of the spectra. Certain spectra which would appear if the lattice were simple cannot appear if it is centred. These spectra are those for which $(h + k + l)$ is odd. It is evident at once that the one lattice centering the other halves the spacings of the planes parallel to the cube faces, so that (100), (300), (500) . . . , and the corresponding spectra from the other cube faces, cannot occur, for halving a spacing always causes the odd orders corresponding to the original spacing to vanish. It will be seen that these are special cases of the general condition for absent spectra deduced above. It is important to notice, however, that, in determining the space-lattice, attention should be directed to the general spectra, for which none of the indices h, k, l , is zero. Halvings of planes for which one or more of the indices is zero can occur for other reasons, as we shall see below. If the lattice is body-centred, not only spectra of the type (100), (300) . . . etc., must vanish, but also (111), (333), (555) . . . , (221), (223) . . . , and so on.

In a similar way, a face-centred cubic lattice can be considered as consisting of four interpenetrating simple cubic lattices, and calculation of the structure-amplitude shows that no spectra can occur for which the indices are partly odd and partly even, but only those for which they are all even or all odd. For each space-lattice there are characteristic absences of spectra of general type, and from these the space-lattice is determined.

THE DETERMINATION OF THE SPACE-GROUP

Just as a space-lattice is characterized by absences of spectra of a general type, so the space-group is characterized by absences of spectra of special types. In a work of this nature, we cannot do more than indicate

the principles underlying the determination of space-groups. We shall again consider a structure based on a simple orthorhombic space-lattice, with each point of which is associated a crystal unit. The existence of a lattice of this sort is shown, as we have seen, by the fact that spectra of all general types occur. Suppose now that perpendicular to the (100) face of the lattice we add a 2-fold screw axis. The existence of such an axis necessitates the existence of other units of structure, derived from those already present by a rotation of

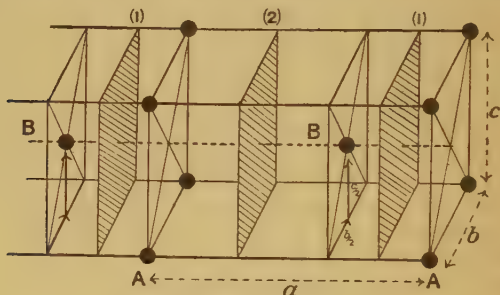


FIG. 23

Illustrating the effect of a glide plane.

The shaded planes (1) are glide planes parallel to (100), with a translation $b/2 + c/2$. They turn the points A into the points B, thus halving the b and c spacings. It will be seen that the presence of the glide planes (1) necessitates the existence of the glide planes (2) half-way between them.

180° about the axis, and a translation, parallel to it, of half the a spacing. A set of planes is thus interleaved half-way between the (100) planes of the lattice, the a spacing is halved, and the spectra (100), (300), . . . , corresponding to the space-lattice, vanish. In general, a 2-fold screw axis must halve the spacing of the lattice in a direction parallel to itself. In a similar way, glide planes of symmetry produce characteristic halvings. A glide plane parallel to (100), with a glide of $b/2$, must halve the b , or (010), spacing: if the glide is $b/2 + c/2$, both the b and c , or (010) and (001),

spacings are halved (Fig. 23). Glide planes and screw axes are always parallel to special directions in the lattice, so that it is the spectra with some indices zero which are affected by them, and it is this fact which makes it important to consider the general spectra in determining the **space-lattice**. Space-groups exist, which are still based on a simple orthorhombic lattice, for which (100), (010) and (001) are all halved by the action of glide planes and screw axes, and all the odd orders from these planes must be absent: but all the general spectra will still occur, as they should for a simple lattice.

For each of the 230 space-groups the characteristic absent spectra have been worked out, and they are tabulated in such works as those of Niggli, and Astbury and Yardley, which also give all the symmetry elements of the groups. If it is known to which of the 32 crystal classes the crystal under examination belongs, it is generally possible to determine the space-group uniquely from the absent spectra. If the class is uncertain, there may still be some doubt. For example, all crystals give identical reflexions from opposite faces, although these faces may have different properties. In other words, polar and non-polar classes cannot be distinguished by X rays, and unless the crystallographic evidence can decide between them, there will be doubt as to the space-group.

THE LIMITATIONS OF PURELY GEOMETRICAL METHODS

At this point it will perhaps be of advantage to summarize the results we have so far obtained. We have seen that the external forms and symmetry, and the general physical properties of crystals suggest that they are built up by the repetition of similar units in a 3-dimensional pattern. Crystallographers had recognized this, and had worked out completely the geometry, and possible symmetry of such patterns. A test of the theory became possible with the discovery of the diffrac-

tion of X rays by crystals. It was found that the diffraction effects which occur are precisely those to be expected from a 3-dimensional lattice, and this provided at once a way of measuring the actual intervals in which the pattern in a crystal repeats itself. It became plain that the units of the pattern were of atomic or molecular dimensions, and the possibility was opened up of determining in detail the arrangement of the atoms in solid bodies. Let us see how far the arguments of the preceding chapters have led us toward this end.

We have seen that, if suitable material is available, we can always determine the size of the unit cell, using for example, the rotating crystal method. Once the size and the axes of the unit cell have been fixed, we can determine the **space-lattice** upon which the structure is based, by examining a large number of spectra, and noticing systematic absences of spectra of a general type. Again, by looking for absences of spectra of special types, having one of the indices zero, it is usually possible to determine the **space-group**, the scaffolding of symmetry planes and axes upon which the structure is built. For determining the space-lattice and space-group, rotation photographs are generally used. The size of the unit cell, and the density and chemical composition of the crystal, enable us to determine the number of atoms in the unit of structure, and this, together with a knowledge of the space-group, often allows us to limit the possible positions of the atoms. To any position in the unit cell there correspond a number of equivalent positions, derived from the first by the symmetry operations of the space-group. Let us suppose, for example, that this number is eight. Now if we find that there are only four atoms of a given kind in the unit cell, it is evident that they cannot lie at the most general positions, but must lie in some special positions whose equivalence is only four. Such special positions will be on symmetry centres, reflexion planes, or 2-fold rotation-axes: for the image of a point lying on a reflexion plane coincides with itself; if the

point moves off the plane, it immediately becomes two points, one the reflexion of the other, and similar considerations apply to the 2-fold axis and the symmetry centre. In this way it is often possible to limit the positions of the atoms considerably, but it is not, in general, possible to fix them. An atom in space requires three co-ordinates, or **parameters**, to fix it. By determining that it must lie on a definite plane or axis, we reduce this number to two or one respectively, but, so far as symmetry alone is concerned, the atom may lie anywhere on the plane or axis, and the remaining parameters may have any values.

Up to this point, the whole process is a geometrical one. There are difficulties, but they are difficulties of technique, and not of principle. Given suitable material, so that the spectra may be observed adequately, it is always possible to determine the unit cell, and generally the space-group. It is, however, the task of X-ray crystallography to find the exact positions of the atoms, and at this point the subject ceases to be a branch of geometry, for we have seen that such a determination must depend on a knowledge of the intensities of the spectra, and both in measuring, and in interpreting these, difficulties not of a geometrical, but of a physical nature, arise, and it is with these that we must now concern ourselves.

CHAPTER IV

THE INTENSITIES OF X-RAY SPECTRA

MEASUREMENT OF INTENSITIES

MEASUREMENTS of the intensities of X-ray spectra can be made most accurately by means of the ionization spectrometer, if a crystal with well-developed faces, or such that faces can be ground on it, is available. The crystal is mounted on the table of the instrument, and the slits between it and the X-ray bulb are closed, until the whole of the incident beam falls on the crystal face. The ionization chamber is set in the correct position to receive the spectrum whose intensity is required, and the slits at the entrance to the chamber are opened to such a width that they receive the whole of that spectrum. If we keep the chamber fixed, and rotate the crystal, we shall find that, although the reflexion is strongest at a certain setting, it is not confined to that setting, but takes place over a certain range of angles on either side of it. This is partly because the incident beam is slightly divergent, but mainly because few crystals even approach the mathematical perfection of the space-lattice over the whole of their bulk. Most crystals are made up of a mosaic of crystal blocks, all approximately parallel, but with a distribution in orientation over a range varying from a few minutes to a considerable fraction of a degree from the mean. As the crystal is rotated, these blocks come in turn into the correct position to reflect and there is no one definite reflecting position. We cannot take the reflexion at the optimum setting as a measure

of the intensity, for this will vary from specimen to specimen of the same crystal, since it evidently depends on the degree of parallelism of the different blocks, or on the state of perfection of the crystal. To get over this difficulty, we measure the total ionization produced in the chamber when the crystal is rotated with uniform angular velocity through the range of angles over which it reflects. If E is the total energy reflected as the crystal is swept with uniform angular velocity ω through the reflecting range, the product $E\omega$ is constant for a given intensity of incident beam, for, if we double ω we halve E , since each crystal fragment has only half the time in which to reflect. Let I be the total energy incident in one second on the crystal, which can be measured by removing the crystal, and allowing the direct beam to enter the chamber for a known time. Then the ratio $E\omega/I$, which is called the **integrated reflexion**, and is usually denoted by ρ , is taken as a measure of the intensity of the spectrum. The integrated reflexion is found to be independent, within certain limits which will be discussed later, of the precise state of perfection of the crystal, and it is this quantity, or something which is equivalent to it, which is meant when the intensity of a spectrum is spoken of. The direct beam from a bulb with a target made, for example, of molybdenum contains, in addition to the characteristic radiation, a considerable amount of continuous radiation of all wave-lengths, which must not, of course, be included in the measurement of I . In absolute determinations, therefore, it is necessary to reflect the direct beam first of all from a suitable crystal, calcite is generally used, and to use this reflected beam, which will be monochromatic, as the incident beam for the intensity measurement. Unless very great power is used, the twice reflected beam is so weak that it is only possible to make absolute determinations of strong spectra. In practice, it is usual to employ the direct beam, and to compare all the intensities measured with the intensity of a standard spectrum, such as the (400)

spectrum of rock-salt, which has been measured absolutely. The value of $E\omega/I$ for NaCl (400) is about 10^{-4} , although it varies somewhat from specimen to specimen of the crystal. There are many experimental conditions to be observed if good results are to be obtained in intensity measurements: we must, however, be content here with this brief description of the principles of the method.

It may not be convenient to cut a face for all the spectra which are needed for a determination. A very useful method is to use a thin slip of the crystal, and to reflect, through it, from planes which are at right angles to the plane of the slip. Suppose, for example, that the plane of the slip is perpendicular to the c axis. Then all the planes ($hk0$) will be perpendicular to the slip, and by rotating the latter in its own plane, each can be brought in turn parallel to the axis of the spectrometer, and the intensities of the different spectra can be compared. If one of them has been measured absolutely, then the intensities of all are known, since all have been measured through a slip of the same thickness. This method is only applicable to crystals whose absorption coefficient for the rays used is small.

PHOTOGRAPHIC METHODS

It is often impossible to obtain crystals of the material under investigation which are suitable for the spectrometer method of intensity measurement, and it is of course important to be able to get some idea of the intensities of the spectra in this case also. If a photographic method, such as the powder method, or the rotating crystal method, is used, an estimate of the relative intensities can be made by comparing the blackening of the film or plate produced by the different spectra, either visually, or better, with some form of photometer. No really satisfactory method of general application has been devised for obtaining absolute intensities photographically, although a large amount of work has been done. The subject is of great import-

ance for the future development of structure determination, but we must be content here with this brief reference.

THEORETICAL FORMULÆ FOR INTENSITIES OF REFLEXION

Any formula for the intensity of a spectrum must contain factors of two types, one depending on the nature of the atoms in the unit cell and their arrangement, and the other on the condition of the crystal and the method used in observing the spectrum.

The condition of the crystal is of great importance. Darwin, as early as 1914, showed that a crystal whose atoms were arranged in mathematically exact array would reflect X rays totally over a small range of angles, of the order of a few seconds, and that the reflexion would be complete in the first few tens of thousands of lattice planes.¹ Experiment shows, however, that, from nearly all real crystals, the reflexion is perhaps twenty or thirty times stronger than that to be expected from Darwin's perfect-crystal formula. The reason for this was pointed out by Darwin himself. Natural crystals are not as a rule mathematically perfect over any considerable volume. It is more correct to regard them as mosaics of more or less perfect blocks, which, although nearly parallel, may vary in orientation over a small range of angles. It is possible to carry out the calculation for the intensity of reflexion from a crystal supposed to consist of blocks so small that there is no appreciable absorption of the rays in any one of them. A crystal of this type is called by Ewald a 'mosaic' crystal. It is easy to see that the intensity of reflexion from a mosaic crystal will be much greater than that from a perfect crystal of the same kind, for in the latter, the reflexion all occurs in the first few thousand layers,

¹ This result is arrived at by taking into account the interaction of each atom with the radiation scattered by the others, instead of treating each as an independent scatterer. This is necessary, because, in a perfect crystal, there will be definite phase relationships between the radiation scattered by the different atoms.

which screen the lower layers during reflexion. When the angle of reflexion is passed, the rays again penetrate more deeply, but, since the lower layers are exactly parallel to the upper ones, their chance of reflecting is gone. In the mosaic crystal, since the different blocks are not all exactly parallel, each gets its chance of reflecting in turn.

Real crystals are neither ideally perfect nor ideally mosaic. The individual perfect blocks of the mosaic may be so large that the upper layers screen the lower ones **in the same block**, and even if this does not occur, some of the lower blocks will be parallel to the upper ones, and will thus be screened during reflexion. These effects are known as **primary** and **secondary extinction**, respectively, and both increase the apparent absorption coefficient of the crystal for X rays during reflexion. Most crystals approach much more nearly to the mosaic than to the perfect type, and it is usual to employ the mosaic formula, and to apply an estimated correction to the absorption coefficient to allow for extinction. It would lead us too far to discuss this correction: no method yet devised is entirely satisfactory, and extinction is the greatest difficulty in the way of interpreting quantitative crystal measurements. It affects strong spectra much more than weak ones. Extinction can be avoided by using powdered crystals, but this is not always practicable.

For reflexion from a crystal face, the mosaic formula for the integrated reflexion is

$$\frac{E\omega}{I} = \frac{N^2\lambda^3}{2\mu \sin 2\theta} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot |S|^2 \quad . \quad . \quad (10)$$

In this formula, N is the number of crystal units in unit volume of the crystal, λ the wave-length of the X rays, μ the linear absorption coefficient of the rays in the crystal, corrected if necessary for extinction, and θ the glancing angle of reflexion. The factor $(1 + \cos^2 2\theta)/2$ allows for the fact that the incident radiation is unpolarized. S is the ratio of the average amplitude

scattered in the direction of the spectrum considered to the amplitude of the incident radiation.

THE ATOMIC SCATTERING POWER AND ITS CALCULATION

We have seen above how it is possible to measure the absolute value of the integrated reflexion. If the value so obtained is substituted in formula (10), S , the amplitude scattered by a single crystal unit, may be calculated, and by comparing this 'observed' S with the values calculated from different assumed atomic arrangements, the structure of the crystal may be determined. Our next task, therefore, is the theoretical calculation of S .

We must suppose the scattering to be done by the electrons in the atoms. Let us take as the unit scattered amplitude that scattered by a single classical electron, that is to say, one which scatters according to the formula of Sir J. J. Thomson. We are not concerned for the moment with the question as to whether or not such an electron exists; we merely take it as a convenient unit. If the crystal unit consisted of a single electron of this type, the factor S would be e^2/mc^2 , e being the charge on an electron expressed in electrostatic units, m its mass, and c the velocity of light. We may take the amplitude, S , scattered by the actual unit in the direction considered as F times that scattered by a single electron, or Fe^2/mc^2 . F is a dimensionless number, and is a function of θ , depending both on the distribution of electrons in the individual atoms, and on the arrangement, or parameters, of the atoms themselves.

Suppose now, that the average amplitude scattered by a single atom of a particular kind in the unit is f times that scattered by a classical electron. The total amplitude, F , scattered by the whole unit is obtained by adding together the contributions from the single atoms, taking into account the phase differences introduced by their distribution in the unit cell. We have already seen, in Chapter III, how this allowance for

phase is made, and it will be evident from formula (8) that we may write

$$F^2 = (f_A \cos \phi_A + f_B \cos \phi_B + \dots)^2 + (f_A \sin \phi_A + f_B \sin \phi_B + \dots)^2$$

where $f_A, f_B, \dots$ are the scattering powers for the atoms of kind A, B, $\dots$.

Just as the value of F depends on the distribution of the atoms in the unit cell, so f depends on the distribution of the electrons in the atoms. Let us consider an atom of atomic number Z as consisting of a cloud of Z classical electrons surrounding the nucleus. It is the region occupied by these electrons which constitutes the main bulk of the atom, and from which the X-ray scattering takes place. The diameters of the atoms are of the same order of magnitude as the spacings of the crystal planes, and are in general several times the wave-length of the X rays. It will therefore be necessary to take into account the phase differences between the contributions to the scattered beam from electrons in different parts of the atom.

We are of course only concerned with the average scattering from a huge number of atoms, and we shall suppose an average atom of the kind considered to have spherical symmetry, an assumption which is justified by experiment. We may define the average electron density in the atom in the following way. Let $U(r)dr$ be the probability of finding an electron between radii r and $r + dr$ from the centre on the atom. Then $U(r)$ is called the **radial electron-density**, and, since the atom is supposed to be spherically symmetrical, it is a function of r only. $U(r)dr$ gives the average number of electrons lying between distances r and $r + dr$ from the centre of the atom, and we must therefore have
$$\int_0^\infty U(r)dr = Z, \text{ the total number of electrons in the atom.}$$

Suppose the atom to lie with its centre at 0 (Fig. 24) on a crystal plane, and consider its contribution to a spectrum formed by reflexion at a glancing angle θ

from the plane. It is clear that the radiation contributing to this spectrum has been scattered by the atom through an angle 2θ . The radiation scattered by an electron at A, distant x from the plane, differs in phase from that scattered by electrons lying in the plane by $4\pi x (\sin \theta)/\lambda$. Now x may be greater than λ , so that the phase difference between the contributions to the scattered beam from different parts of the atom may be considerable, if the angle θ is at all large. If $\theta = 0$, all the scattered components have travelled equal paths. The contributions from all the electrons are then in phase, and the total scattered amplitude is Z times that

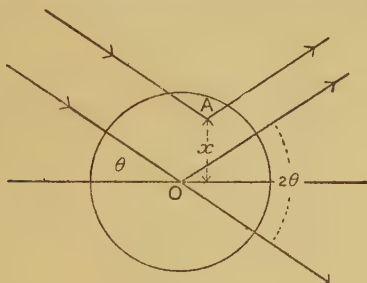


FIG. 24

The scattering of radiation from an atom.

scattered from a single electron in the same direction, but as θ increases, the phase difference increases also, the contributions from the different parts of the atom no longer co-operate, and the total amplitude scattered is less than Z times that due to a single electron. The factor f therefore approaches the total number of electrons in the atom for small angles of scattering, but decreases rapidly as the angle of scattering increases.

THE f -FACTOR AND WAVE MECHANICS

In order to calculate f theoretically, we need to know $U(r)$, the radial electron density. Now we have expressed $U(r)$ in terms of classical electrons, and we

know from the existence of the Compton effect that electrons do not scatter X rays entirely according to classical laws. According to the wave mechanics, instead of thinking of point electrons, describing orbits in the atom, we must consider a wave-function, ψ , a solution of Schrödinger's equation, associated with each point of the atom, and such that $|\psi|^2 dv$ is proportional to the chance of finding an electron in an element of volume dv at the point considered. The quantity $|\psi|^2$ may thus be thought of, in a sense, as the average charge density at any point in the atom, and the quantum theory of scattering shows that, to a close approximation, with radiation of the frequency we are considering here, we may obtain the **coherent** scattering from the atom, that is to say, the scattered radiation which can interfere and produce X-ray spectra, as distinct from the incoherent Compton radiation which cannot, by treating the quantity $|\psi|^2 dv$ for each element of volume of the atom as an element of classically scattering charge. Thus we may replace the hypothetical distribution of classical electrons, in terms of which f was defined, by the Schrödinger charge-density distribution for the atom. We may in fact put $U(r)$ equal to $4\pi r^2 |\psi|^2$, and carry out the calculation of f exactly as if $U(r)$ were a classical distribution of charge. It is quite easy to show that, for such a distribution,

$$f = \int_0^\infty U(r) \frac{\sin \phi}{\phi} dr, \text{ where } \phi = 4\pi r(\sin \theta)/\lambda \quad . \quad . \quad (11)$$

Now Hartree has devised a method of calculating the approximate numerical value of $|\psi|^2$ for any point of an atom. If then the theory outlined above is correct, we have a means of calculating f for an atom, and hence, F for any arrangement of atoms.

EXPERIMENTAL TEST OF THE THEORETICAL FORMULÆ

It is evidently important to test the theories given above by direct experiment. This has been done by studying quantitatively the reflexion of X rays from

certain simple crystals, in which the positions of the atoms are fixed by symmetry, with no undetermined parameters. In rock-salt, which is one of the crystals which was used for this purpose, the Na and Cl atoms lie on two interpenetrating face-centred cubic lattices, and only spectra with indices all odd or all even occur. For spectra with even indices, $F = f_{Cl} + f_{Na}$, and for those with odd indices, $F = f_{Cl} - f_{Na}$. Accurate absolute measurements of the integrated reflexions for a number of spectra were made, and from these the values of F were calculated, using formula (10), and putting $S = Fe^2/mc^2$. The values of F , plotted as a function of θ , lay on two smooth curves, one giving $f_{Cl} + f_{Na}$, the other $f_{Cl} - f_{Na}$. By taking half the sum and half the difference of the ordinates of these curves, f_{Cl} and f_{Na} could be obtained separately as functions of θ . The results were evidently of the right order: the total number of electrons in the two atoms is 28, and $f_{Cl} + f_{Na}$ was about 21 at the smallest angle of scattering at which reflexions were measured, about $12^\circ 30'$, and was increasing with decreasing angle; but before a proper comparison between theory and experiment could be made, it was necessary to allow for the thermal motions of the atoms.

THE TEMPERATURE FACTOR

Values of f calculated from theoretical charge distributions will of course refer to the atom at rest; the atoms in a crystal are not, however, at rest, but in a state of thermal vibration. The higher the temperature, the greater the average distance of the electrons in an atom from the lattice planes, and the more rapidly, therefore, the value of f dies away with increasing angle of scattering. If each atom be supposed to vibrate as a whole, it can be shown that $f = f_0 e^{-M}$, where f_0 is the value of f for the atom at rest, and

$$M = 8\pi^2 \overline{u^2} (\sin^2 \theta) / \lambda^2 \quad . \quad . \quad (12)$$

$\overline{u^2}$ being the mean square displacement of the atoms

from the average position of the planes at which reflexion is taking place at a glancing angle θ . Debye and Waller have given expressions for u^2 , for simple crystals, in terms of the temperature, and known quantities, such as the specific heats and elastic constants, so that for such crystals it is possible to calculate the value of M .

Experiments on the variation with temperature of the intensity of reflexion of X rays from NaCl showed that, from about 500° abs. down to the lowest temperature used, that of liquid air at 86° abs., the observed temperature factor agreed excellently with that calculated from Waller's theory. This being so, it seems justifiable to extrapolate further, and to calculate from the observed values of f , the values at the absolute zero. We must not, however, assume that the values so calculated are those for the atom at rest. The wave-mechanics requires that the atoms in a lattice should possess, as Planck had already suggested, half a quantum of vibrational energy for each degree of freedom, even at the absolute zero, and it will therefore be necessary to apply a further correction to the f values corrected to this temperature, in order to allow for the existence of this zero-point energy. It is possible to make this correction, and, by so doing, we obtain a set of values of f_0 which can be compared with those calculated theoretically.

The values of $U(r)$ for Na^+ and Cl^- were calculated by Hartree from the wave-functions of the atoms,¹ and in Fig. 25 they are shown, plotted against the atomic radius r . From these, the values of f_0 were calculated by integrating equation (11) numerically. The theoretical f curves for Na^+ and Cl^- are shown by the full lines in Fig. 26; the circles in the same figure

¹ The wave functions and the theoretical values of f are calculated on the assumption that the atoms are ionized. This, as we shall see in Chapter V, is probably the case in the rock-salt lattice. For the ions, the total number of electrons is 10 for Na^+ and 18 for Cl^- .

represent the observed values of f , corrected, as just described, with allowance for zero-point energy, and the crosses, the same values without the allowance for

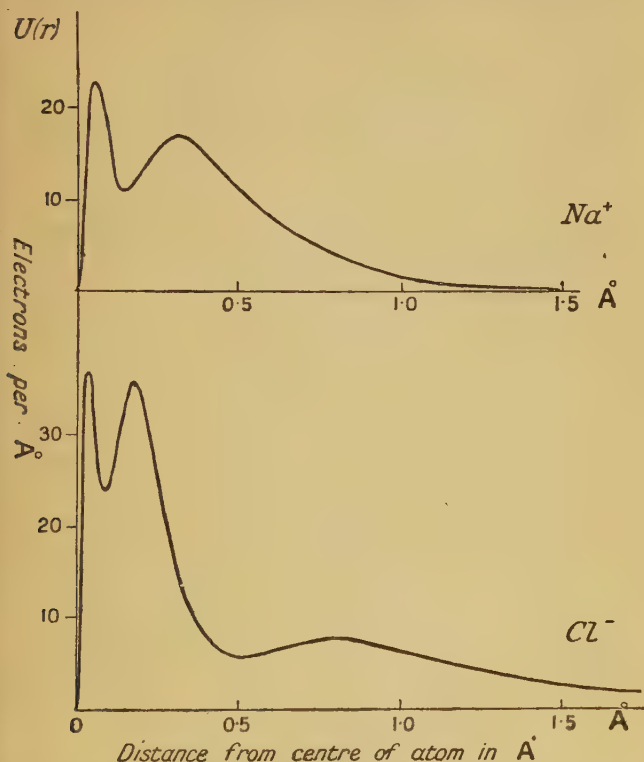


FIG. 25

Radial distributions of charge density in Na^+ and Cl^- . (Hartree.)

zero-point energy. It will be seen that the agreement between theory and experiment is, on the whole, excellent if zero-point energy be assumed. Equally good

agreement has been obtained with similar experiments on KCl and Al, and, so far as the evidence goes at present, the theory given above appears to be confirmed.

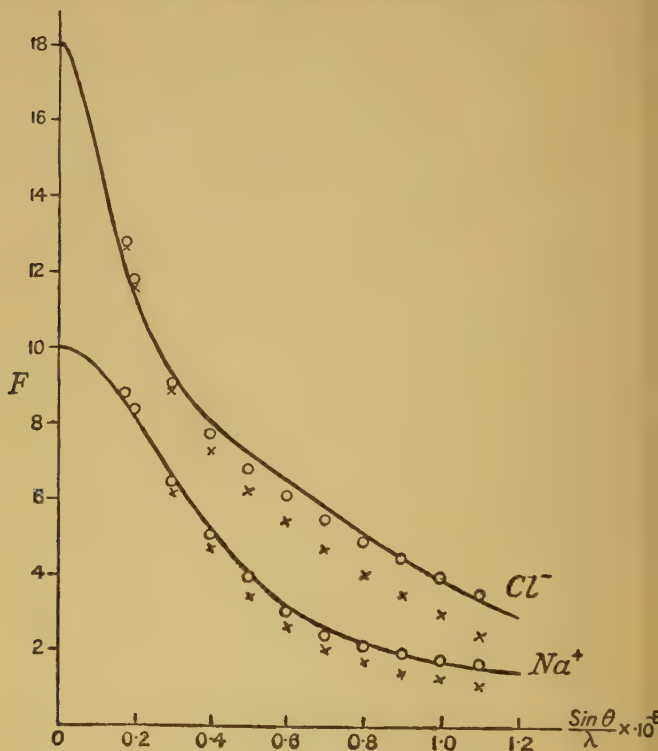


FIG. 26

Comparison of theoretical and experimental f curves. The continuous lines are the f curves calculated from the Schrödinger charge-density distributions for the atoms at rest. The circles and crosses are the observed values corrected for temperature with and without allowance for zero-point energy.

quantitatively by experiment, and can therefore be used with some confidence as a basis for structure determination.

THE AMPLITUDES OF THE ATOMIC VIBRATIONS

From the values of M , it is possible to calculate directly the root-mean-square displacements of the atoms from their mean positions. The following values are obtained at room temperature. In NaCl, Na, 0.24 Å, Cl, 0.22 Å; in KCl, K and Cl, 0.25 Å; in Al, 0.17 Å. At the absolute zero, the amplitudes in NaCl and KCl are still about 0.1 Å, a by no means negligible fraction of the lattice spacings.

DETERMINATION OF THE ATOMIC PARAMETERS

We are now in a position to discuss the determination of the parameters of a crystal structure. The intensities of as large a number of spectra as possible are determined, preferably absolutely, and the corresponding values of F are calculated from the formula for the intensity of reflexion. These values are compared with those calculated from different assumed atomic arrangements, using values of the f -factors for the individual atoms, either calculated theoretically by some method such as that of Hartree, or based on observations made on other crystals. The method is essentially one of trial and error, different atomic arrangements being tried in turn, until one is found which gives satisfactory agreement between the observed and calculated F 's over a range so large that it cannot well be accidental. For crystals with one or two parameters, quite a few trials are generally enough to fix the structure, but if, as is often the case, there are ten, twenty, or even more parameters, the problem could not possibly be solved in this way, unless certain considerations limited the choice of co-ordinates, and enabled parameters not far from the truth to be guessed at the outset.

Important, among such considerations, is the idea of atomic size. Information obtained from structures which have been determined shows that each kind of atom in a crystal structure occupies a certain definite amount of room. Proposed structures, which are quite

possible so far as symmetry alone is concerned, but in which the atoms have not sufficient room, can thus be discarded at once, and this frequently limits the possible arrangements very greatly, and may sometimes almost determine the structure. It must be remembered also that a crystal is statically stable. If the structure is composed of positive and negative ions, their distribution is likely to be such that each ion is surrounded so far as possible, by those of opposite sign. It is a very noticeable fact that, when models of structures which have been determined are made, they look stable and reasonable. The question of co-ordination is also very important. Certain atoms are nearly always surrounded by the same number of atoms of a given other kind arranged in the same way.

By such methods, the skilled worker is able to narrow down the field of possible structures before making any actual tests, but it must be emphasized that such procedure is only provisional, and does not determine the structure. The final determination can only be made by obtaining agreement between the observed and calculated F values. For solving really complicated structures, the importance of knowing F absolutely cannot hardly be exaggerated. If it can be said that the scattering power of the crystal unit, in a given direction is about equal to that of so many electrons, one has a definite piece of information which is of far more value than the mere knowledge that the spectrum is strong or weak on some arbitrary scale.

ANALYSIS BY FOURIER SERIES

It would evidently be far more satisfactory if the structure could be obtained directly, without this process of trial and error, and a method, suggested originally by Sir W. H. Bragg, but developed in detail by Duane, Compton, Havighurst and W. L. Bragg, appears at first sight to make this possible. A crystal structure has a 3-dimensional periodicity, and the density of scattering matter at any point in it must therefore be expressible

as a triple Fourier series. There is one term in the series for each spectrum, its coefficient being the corresponding value of F . By measuring F , therefore, for a large number of spectra, and substituting the values in the series, it would appear to be possible to obtain the electron density at any point in the crystal, and hence its structure. There are, however, difficulties.

In the first place, to evaluate the triple series for a number of points sufficient to give the structure would be an immense labour, and would, moreover, involve the measurement of a very large number of spectra. This difficulty may be avoided, to some extent, by supposing the structure projected on three faces in turn. The series for the projections are double ones, and can be evaluated without excessive labour, and this method has been developed, and used with success, by W. L. Bragg. There is, however, a more fundamental difficulty. By measurement we can only obtain F^2 , so that the **signs** of the Fourier coefficients, or, more strictly, the relative phases of the spectra, remain undetermined. It is not therefore possible to evaluate the series unless the structure is already known accurately enough to determine the signs of the coefficients in advance. The method is thus not so direct as it appears to be at first sight, but it may nevertheless be of considerable value in shortening the work of finding accurate values of the parameters. It may be said, indeed, that, in the Fourier method, as in the method of trial and error, there is no standard procedure. Each crystal is a separate problem, and the success obtained in determining its structure depends largely on the skill and experience of the worker.

CHAPTER V

TYPES OF CRYSTAL STRUCTURE

SIMPLE METALLIC AND IONIC CRYSTALS

IN this chapter we shall consider, very briefly, some of the more important results of crystal analysis. Space will not permit of a detailed description of any particular structures, and we must confine ourselves to the discussion of some of the broader principles which appear to govern the building of crystals. One of the most interesting points is the importance of purely geometrical, as distinct from chemical, considerations. To a close approximation, we may regard each atom as a sphere of definite radius, and may consider crystals to be formed by packing such spheres in the most stable and economical manner. Naturally a statement of this kind requires much qualification, but, as a broad generalization, it is of great importance, and explains many of the salient facts of crystal structure.

In crystals of the metallic elements, the arrangement of the atoms is often simply that of an assemblage of spheres packed as closely as possible. Two types of close-packing are of special importance. Suppose, for example, that we are piling balls on a table, and that the first layer has been completed. If the balls in this layer are tightly packed, their centres will lie at the corners of a network of equilateral triangles. The balls of the second layer must now be placed so as to lie in the hollows of the first layer, and those of the third layer in the hollows of the second. Each layer is, of course, exactly similar, but, in considering the structure

as a whole, we see that there are two possibilities for the balls of the third layer : they may be placed exactly over those of the first layer and the structure may then be continued so that pairs of layers repeat indefinitely ; or they may be placed neither over the balls of the first layer, nor over those of the second layer, the structure being continued by placing the fourth layer over the first, the fifth over the second, and so on, so that the arrangement of three layers is repeated. The first type of arrangement has hexagonal symmetry. The second has cubic symmetry, and an examination of a model built in this way will show that the centres of the balls lie on a **face-centred** cubic lattice. The packing is equally close in the two types of arrangement, every ball being touched by 12 neighbours. Among the elements which have a face-centred cubic, or cubic close packed, structure are Cu, Ag, Au, Ca, Al, Pb, and Pt. The hexagonal close packed structure is exemplified by Be, Mg, Zn, Cd, Ru, and Os. Not all metallic elements crystallize in a close packed structure. Li, Na, K, Cr, Mo, W and the ordinary modification of Fe, as well as a number of others, have a body-centred cubic structure, while others, among which may be mentioned Sb, Bi and Mn, have structures of more complicated types.

It is in the simple inorganic compounds that the geometrical relationships of crystal structure are best shown. The atoms in such crystals are almost certainly ionized, and for this reason they are often called *ionic* crystals. In NaCl, for example, we may suppose that the Na atom has lost its outer electron, and so has acquired an excess of positive charge, while the Cl atom has absorbed the electron lost by the Na atom into its structure, completing the M electron group, and at the same time acquiring an excess of negative charge. Two such ions will attract one another, because of the electrostatic forces between their excess charges, but they cannot approach to within less than a certain distance, owing to the strong forces of repulsion which must set in when their outer electron shells come into close

proximity. When the centres of the two ions come within a certain distance of one another, attraction and repulsion balance, and they can approach no closer. The repulsive forces increase very rapidly with decreasing distance, once they have become appreciable, so that even a very large increase in the attractive force cannot pull the ions much closer together, and it is in this sense that we must think of them as possessing a definite radius.

We may think of the simple inorganic compounds as built up of such oppositely charged ions, each with its appropriate ionic radius. In order to reduce the electrostatic energy to a minimum, each ion will, so far as possible, surround itself with ions of the opposite sign, but it appears also to be a condition of stability that the anions and cations should touch each other in the sense explained above. Suppose, for example, that a crystal of type AX, A and X being oppositely charged ions, has a structure such that the ions A lie at the centres of cubes formed by the ions X, and the ions X at the centres of cubes formed by the ions A. In such a structure, each ion has eight ions of the opposite sign around it; in other words, the co-ordination number is eight, which is the highest possible for a crystal with equal numbers of the two kinds of ion. Now, merely as a matter of geometry, unless the ratio of the radius of A to that of X is greater than 0.73, the X ions will touch one another along the cube edges and the A ions will, so to speak, 'rattle' inside the cubes of X ions without touching them. Now structures of this kind appear to be unstable, and if the ratio of the radii becomes less than 0.73 the crystals tend to have the rock-salt type of lattice, in which each ion is surrounded by only six of the opposite sign, but in which the anions and cations are again able to touch one another. The alkaline halides provide an interesting example of this. CsI, CsBr and CsCl, in which the radii of the two ions are nearly equal, crystallize in the first of the two forms discussed above, with a co-ordina-

tion number of eight, but all the others have a rock-salt structure, with a co-ordination number of six. Most of the oxides and sulphides, and some of the selenides, of the bivalent metals also have a rock-salt structure. If the ratio of the ionic radii is less than

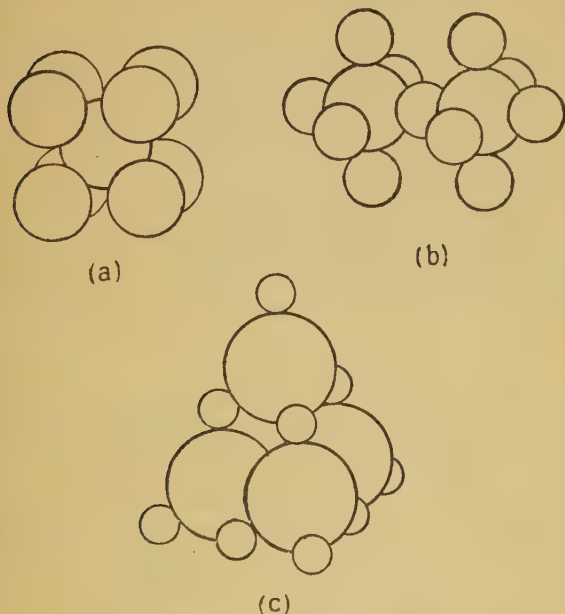


FIG. 27

Types of co-ordination in binary ionic compounds.

- (a) Caesium chloride type.
- (b) Rock-salt type.
- (c) Zinc-blende type.

0.41, the larger ions come into contact without touching the smaller ones even in the rock-salt structure. Geometrical stability can again be attained, however, if the co-ordination number sinks to four. This gives the zinc-blende (cubic) or wurtzite (hexagonal) structure,

in which each ion lies at the centre of a regular tetrahedron of ions of the opposite kind. CuCl , CuBr , CuI , BeS , ZnS , ZnSe have the zinc-blende structure, while BeO and ZnO , among other substances, have the wurtzite structure. The CsCl , NaCl and ZnS coordinations are illustrated in Fig. 27.

The purely geometrical account of crystal building which we have given above is of course far too simple and many other factors have to be taken into account. To mention only one: if one of the ions is small and the other large and easily polarizable, the polarization forces become considerable and may modify the structure considerably. CdI_2 is an interesting example of this. The crystal is composed of sheets consisting of two layers of the large polarized iodine ions held together by the small cadmium ions between them. Each sheet is very rigid, but adjacent sheets are only lightly held together, and the crystal has a very perfect cleavage.

COMPLEX IONS

Crystals consisting of a metallic ion and a complex ion, such as CO_3 , NO_3 or SO_4 , have, as a rule, symmetries lower than those of the simple binary compounds, but again the structure appears usually to be determined mainly by the size and shape of the constituent ions. One example of this must suffice. The sulphates of Ba , Sr , and Pb , the perchlorates and permanganates of K , Rb and NH_4 , the selenates and chromates of Sr and Ba , and a number of other compounds of the type XRO_4 , all crystallize in the same way, forming rather complicated orthorhombic structures (Fig. 28). The reasons for this must be mainly geometrical, for the substances differ greatly chemically, and are alike only in being composed of ions of similar size and shape. The RO_4 group, which consists of a tetrahedral arrangement of O around R , is no doubt the determining factor, but the size of the metallic ion is also of importance, for anhydrite, CaSO_4 , with a smaller metallic ion, crystallizes in a different manner. It is perhaps

significant that, while the crystals in this series whose ions are univalent are soluble, those in which they are bivalent are in general very insoluble. It seems likely that this is due to the greater forces between the bivalent

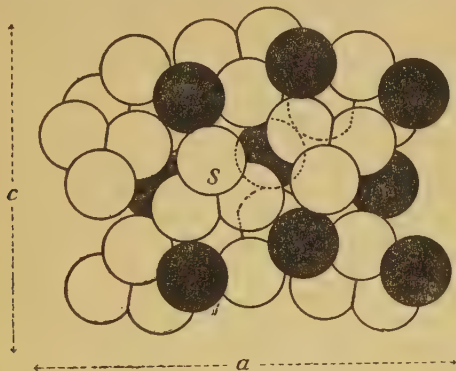


FIG. 28

The barium sulphate structure.

The black circles represent the metallic ions, the white circles oxygen, arranged tetrahedrally about sulphur. Only three of the four oxygen atoms in each tetrahedron are visible, the fourth lying immediately below the atoms of type S.

ions, and illustrates the fact that the physical properties of crystals with similar structures may differ considerably.

THE SILICATES

Some of the gem-stones, and many of the silicates which include a large number of the naturally occurring minerals, are very interesting examples of crystals in which the binding is mainly ionic in character. In these crystals, the most important constituent, oxygen, which is a relatively large ion, is associated with such ions as Si, Al, Be, Mg, and Fe, all of which are considerably smaller. The main bulk of the crystal is occupied by oxygen ions, which are frequently nearly in close-packing, and the smaller ions fit into the spaces

between them, acting as a sort of cement to keep the structure together. In the ruby or sapphire, for example, whose formula is Al_2O_3 , the oxygen ions are in a hexagonal close-packed array, distorted only slightly by the Al ions which are small enough to fit into its interstices. Olivine, MgSiO_4 , and chrysoberyl, BeAl_2O_4 , are also based on a hexagonal close-packed arrangement of oxygen.

The mineral cyanite, Al_2SiO_5 , a triclinic crystal, is a very interesting example. The unit cell contains four molecules of cyanite, and therefore 20 atoms of oxygen, which, taking into account the known ionic radius of oxygen in crystals of this type, 2.7 Å, and the size of the unit cell, must be nearly in close-packing. Now it was noticed by W. L. Bragg that, with oxygen atoms in cubic close-packing, it is possible to select a triclinic cell containing 20 atoms, whose size and shape are almost exactly those of the cyanite cell. It appeared likely, therefore, that the structure consisted of a nearly cubic close-packed array of oxygen ions, the low symmetry of the actual crystal being due to the distribution of the Al and Si in the interstices of the structure, an idea whose essential correctness was verified by examining the X-ray spectra given by the crystal. This is an excellent example of the way in which, by taking into account all the circumstances of the case, it is often possible to get at the structure of a crystal far too complicated to yield to a direct attack.

In some of the silicates, the oxygen, while not close-packed throughout the structure, is locally close-packed, forming a kind of girder structure with comparatively wide-open spaces. Beryl, for example, is a honeycomb structure of close-packed oxygen, with actual holes going right through it.

In every silicate which has been analysed, silicon is found to lie at the middle of a nearly regular tetrahedron of oxygen atoms. Even in the metasilicates, in which the silicon-oxygen ratio is 1 : 3, there is no SiO_3 group. Oxygen atoms are shared by silicon atoms

in such a way as to bring the ratio down to the right value, in some cases, as in beryl, by the SiO_4 groups forming rings (Fig. 29), and in others, as in the pyroxenes and amphiboles, by the groups forming endless chains through the structure. Many of these minerals are fibrous, and the directions of the chains are the same as those of the fibres.

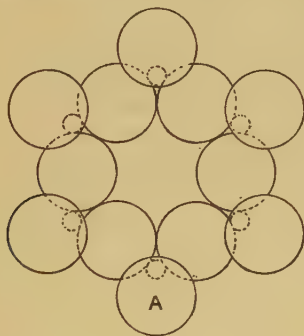


FIG. 29

A ring of SiO_4 groups from the beryl structure.

Oxygen atoms are arranged tetrahedrally about the silicon atoms (small dotted circles), the fourth oxygen atom in each tetrahedron being exactly below the atom of type A. Each oxygen atom in the ring of six is shared between two silicon atoms. There are six silicon atoms and eighteen oxygen atoms in the ring.

MOLECULAR AND ORGANIC CRYSTALS

In the types of structure so far considered, there has been no trace of the chemical molecule. In the rock-salt crystal, for example, each Na atom stands in the same relationship to six Cl atoms, and each Cl atom to six Na atoms, and the whole structure must be considered as a unity. The same is true of the silicate class. Indeed, it may probably be said that, except in the crystalline state, many of the complicated silicates have no distinct existence. In many crystals, however, and particularly in the crystals of the organic compounds, there is a well-defined molecule. The atoms in this

molecule are linked together not by ionic or electrostatic forces, but by some form of co-valent binding, such as that which unites two oxygen atoms in the gas molecule, and the whole crystal is built up of such molecules, held together by the residual forces of attraction between them. Such crystals are, as a rule, much softer, far less rigid in structure, and have lower melting-points than the typical ionic crystal.

The structures of few organic crystals are known in complete detail, and the problem of determining them is of peculiar difficulty. It is often impossible to get well-developed crystals, so that absolute measurements of intensity, upon which the analysis of complicated structures must finally depend, are extremely difficult to make. Then, again, the hydrogen atom, which is often a very important constituent of organic crystals, is such a weak scatterer of X rays that it is almost impossible to determine its position except by inference. In spite of these difficulties, however, good progress has been made, notably by the school of Sir W. H. Bragg, and we already have a fair knowledge of the structures of organic crystals of certain types.

One of the interesting results of the analysis of organic crystals is that the structural formulæ of the organic chemists are seen to have a physical existence. The benzene ring is a ring; naphthalene has a double ring, and the long-chain compounds are really long chains of carbon atoms whose length and configuration can be determined. In the beautiful work of Shearer and of Müller on the fatty acids, the carbon chain can be seen growing link by link as CH_2 groups are added, and its length, and the positions of substituted groups in the chains can be determined. There is also a considerable amount of evidence, based on the structures of a number of methane derivatives, for a tetrahedral linkage to the carbon atom.

Even in inorganic crystals the ionic type of binding is not universal. The non-metallic elements are a case in point. In diamond and silicon, for example, the

atoms are linked together very rigidly, so that each atom lies at the centre of a tetrahedron composed of four others, and the binding between these atoms, which are of the same nature, can hardly be ionic in character. But there is in these cases no evidence of a molecule: unless, indeed, we should think of the whole crystal as a molecule.

CONCLUSION

The science of X-ray crystallography is still in its infancy, and, although considerable progress has been made in the last few years, only comparatively simple structures have as yet been analysed with any approach to completeness, and we are far from the stage at which it will be possible to analyse any crystal whatever, simply as a matter of routine. We are, in fact, slowly learning the technique of a new branch of optics, in which we cannot use lenses, nor form optical images, but must get all our knowledge from the intensity of the light scattered by the object under investigation in various directions, and are, moreover, deprived of all knowledge of the phase of the scattered light, which is what a lens really gives us. To appreciate what this means, we have only to imagine our ordinary vision restricted in this way. It is, in fact, only because the regularity of the structure of a crystal impresses a corresponding regularity on the scattered light that we are able to make any progress at all. Nevertheless, the method has already given us a large amount of information concerning the structure of matter which, only twenty years ago, would have seemed impossible of attainment, and we cannot doubt that this is only a small fraction of the knowledge that it will give us, as the technique becomes more refined, and the principles of X-ray optics are better understood.

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